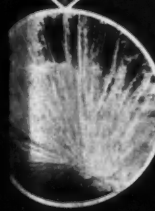


CHEMISTRY



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Editorial:

Civilization Renewable

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Civilization Renewable

► OUR CIVILIZATION and the face of our earth may be capable of lasting more than a few lifetimes. If not, it will be because we are so profligate in using the irreplaceable resources and materials of the earth.

In a few short decades we are using up the underground stores of gas and oil. We dig coal as though it will last forever. The richest iron ore is scooped up by steam shovels as though it were so much dirt. Our copper is almost gone. So are the best of our zinc and lead deposits. We have been living on the unrenovable "fat" of the land.

There are even grave doubts as to whether it will be wise in the long run to use the minute amount of uranium in the earth's crust for the generation of power. Power *can* be had from waterfalls, and the sunshine. Uranium fissioned is gone forever.

War, strife and a declining birthrate have squandered much of the human birthright of the peoples of the western world. But doing something about that is more hopeless and difficult than attempting to salvage the chemical future.

Two major advances in chemistry (see the first two articles in this CHEMISTRY) are the use of corn cobs and oat hulls instead of coal for making nylon, and a practical process for producing alumina from clay. Viewed in the perspective of the spendthrift era in which we live, these achievements are more important than we rich people realize. Extracting magnesium and other chemicals from the almost limitless sea is in the same class.

How soon will we pay our way, energetically, by using the power of the sunshine that floods the earth?

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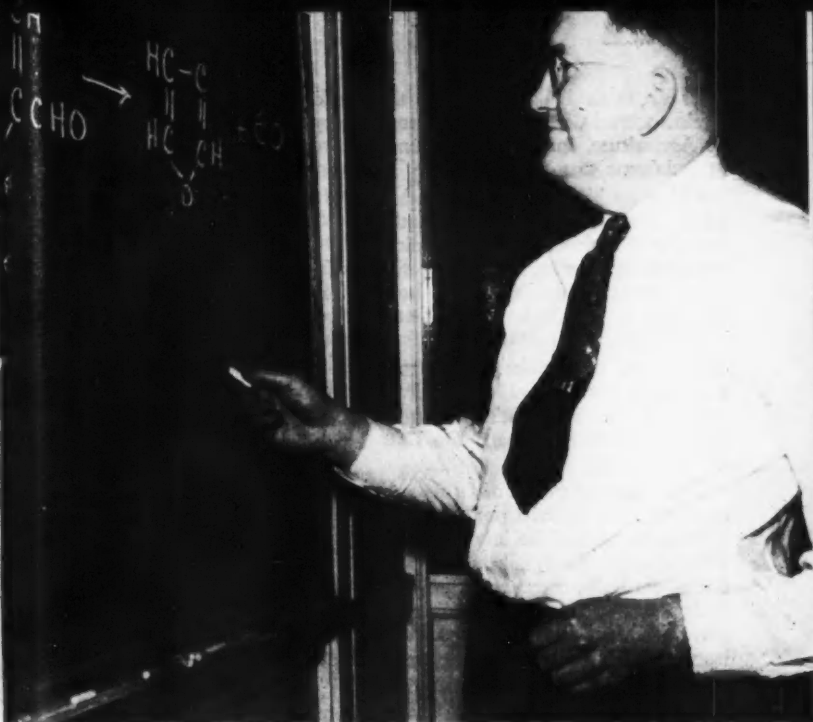
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► FORTY PAIRS of nylon stockings and a bushel of corn cobs, out of which they could be synthesized in large part, might have been a more symbolic illustration, but here is Dr. O. W. Cass, chemist who participated in the accomplishment, ready to explain the furan approach to nylon, as he does in the article beginning on page 2.

Stockings From Corn Cobs

► THOSE LOVELY, sheer nylons—they are going to be synthesized from corn cobs and oat hulls instead of coal, air and water.

Chemists have discovered how to make nylon plastic from waste products from the farm, and Du Pont has begun constructing a new plant at

Niagara Falls to make the chemicals of the new nylon process from furfural, a chemical curiosity of a quarter of a century ago.

"Over 100,000 tons of agricultural by-products will be needed to supply the furfural needed by the new plant," Dr. O. W. Cass, of DuPont's Niagara

MARCH 1947

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Falls Research Laboratory, told the twelfth annual Chemurgic Conference of Agriculture, Industry and Science at Oklahoma City (March 27).

Nylon stockings, panties and other products will be grown down on the farm so far as their basic raw chemical materials are concerned. Now the nylon raw materials are obtained from natural gas, petroleum or coal—and air and water.

"We can now make nylon from materials which are available in practically unlimited quantities because they are grown each year," Dr. Cass explained.

The starting point of furfural, chemical raw material for the new nylon process, may be any one of a wide variety of agricultural by-products—oat hulls, corn cobs, cottonseed hulls, flax shives, bagasse from sugar cane, peanut shells, rice husks or even wood.

One bushel of corn cobs makes 40 pairs of stockings, so far as the basic chemical is concerned, but other chemicals than the principal one are also needed.

A dozen years were required to de-

velop the new nylon process. Laboratory research began in the fall of 1935, three years before nylon was announced to the public. The fundamental nylon process took over a decade of research and pilot plant work.

Two intermediate chemicals that nylon wearers never hear about are combined to produce the finished nylon material. These are called adipic acid and hexamethylene diamine. The conventional process uses phenol or benzene from coal, ammonia from air and water, and oxygen from air.

The new process announced by Dr. Cass starts with the furfural from cobs or hulls, converts it into adiponitrile and then makes hexamethylene diamine.

A new field of chemistry, based on furfural, and called furan chemistry, was predicted by Dr. Cass, who rated nylon production as just one of many future chemical achievements based on utilization of this kind of waste materials.

CHEMISTRY carries the full paper by Dr. Cass because of its interest and importance.

Nylon From Agricultural By-Products

by DR. O. W. CASS

► IN 1938, the Du Pont Company announced to the public a new synthetic material known as nylon. In that year, commercial production of nylon was begun. Nylon appeared on the market first in the form of toothbrush bristles. Two years later, introduction of this new polymer as a hosiery yarn was successful, leading to

the production of over 100 million pairs of nylon hose in 1941. The contributions of nylon to the war, and its steadily expanding production and widening use are well known.

Nylon was the culmination of over 10 years' fundamental research and pilot plant activities carried out by the Du Pont Company, not only on the production of the finished fiber, but

also on the manufacture of the required chemical intermediates for the fiber—namely, adipic acid and hexamethylene diamine—for the production of which no commercial process was available. The processes originally developed made use of phenol, and later benzene (from coal), ammonia (from air and water), and oxygen (from air), leading to the statement that this new fiber was made from coal, air, and water.

Alternative routes to these two chemical intermediates were early investigated by the research organizations of the Du Pont Company. The Electrochemicals Department, with laboratories at Niagara Falls, N. Y., was among those interested. In the fall of 1935, three years before nylon was announced to the public, this laboratory began work on the development of an alternative process for the production of nylon intermediates, using furfural as the major raw material. This work has extended over the past 12 years, and has resulted in the development of a process for the production of adiponitrile—a key intermediate for nylon—from furfural. The construction of a Du Pont plant at Niagara Falls for the operation of this process has begun. Thus, another large-volume utilization of furfural as a chemical intermediate is underway just 25 years after its first commercial production.

As you are all aware, furfural can be manufactured from a wide variety of agricultural by-products—oat hulls, corn cobs, cottonseed hulls, flax shives, bagasse, peanut shells, rice husks—or it may be recovered as a by-product of the wood-fiber industry. The manufacture of furfural was pioneered in

the United States by the Miner Laboratories, and The Quaker Oats Company, and was first offered in quantity on the American market in 1922 at \$2.50 a pound. By 1926, the price had dropped to 15 cents a pound, and in 1936 to approximately 10 cents. Because of the pioneer work of these two companies, technique and experience were available for the expansion of furfural production demanded during the war by the synthetic rubber program.

Hundred Thousand Tons Used

The Quaker Oats Company will supply the furfural needed for this new adiponitrile process as soon as the Niagara Falls plant begins operation. The Quaker Oats Company estimates that over 100,000 tons of agricultural by-products will be utilized annually to supply the maximum amount of furfural the Du Pont Company might need for this process.

As a raw material for chemical processes, furfural possesses many attractive features. It is available in essentially unlimited quantities, and, unlike raw materials derived from natural gas, petroleum, or coal, is "grown" each year, so that no depletion of furfural sources need be feared.

Announcement of this new process for the manufacture of adiponitrile, an important nylon intermediate, starting with the corn cobs or other agricultural by-products as basic raw materials, will probably give rise to the question:

Stockings per Bushel?

"How many pairs of stockings can be made from a bushel of corn cobs?"

The answer is, "None." What the

chemist makes, starting with corncobs, is just one of the chemicals which goes into nylon—an important chemical, but no more important than others needed. From the furfural derived from cobs, oat hulls, or other similar agricultural by-products, the chemist first makes adiponitrile, which is chemically converted into hexamethylene diamine. This, in combination with other important chemicals, is processed into nylon yarn. One bushel of cobs yields enough hexamethylene diamine to go into about 40 pairs of stockings, but it should be emphasized that other chemicals are also needed.

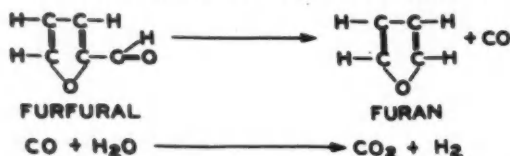
To use corncobs as a basic raw material in nylon manufacture, there must be millions of dollars in plant investment, the technical knowledge and skill of hundreds of highly-trained research and development men, and the work of thousands of others in a great variety of jobs.

The process which has been devel-

oped for the manufacture of adiponitrile from furfural is an excellent example of the intricacies of modern industrial organic chemistry, involving, as it does, the carrying out of four successive complicated organic reactions under carefully controlled conditions to give high yields of the desired product.

The process may be outlined as follows: Furfural is catalytically decomposed to form the 5-atom ring compound furan, which is hydrogenated to the saturated cyclic ether tetrahydrofuran. This compound is reacted with hydrogen chloride to yield 1, 4-dichlorobutane, which is converted to adiponitrile by reaction with sodium cyanide. Adiponitrile is then hydrogenated to hexamethylene diamine. Hexamethylene diamine and adipic acid combine to form nylon salt, which, upon processing, yields the nylon fiber of commerce.

STEP I - ADIPONITRILE FROM FURFURAL



The manufacture of furan from furfural is the first step in this new route to the nylon intermediate, adiponitrile. The manufacturing process involves the catalytic removal of the aldehyde side chain from furfural as carbon monoxide. The reaction is carried out at 400° C. over a catalyst consisting of a mixed chromite of zinc and either manganese or iron (U. S. Patent 2,374,149). The furfural is

vaporized and mixed with steam before passage over this catalyst. The carbon monoxide which is released by decomposition of the furfural reacts with the steam present to form carbon dioxide and hydrogen. Furan, unconverted furfural, and water are condensed from the gas mixture passing from the catalyst chamber, leaving a mixture of equal volumes hydrogen and carbon dioxide as the uncon-

densified gaseous product of the reaction. The conversion of furfural to furan is nearly complete and the yield of furan is high. After some hours operation, the catalyst requires reactivation. This is readily carried out by

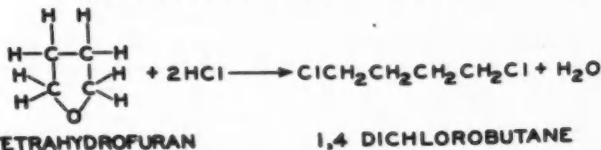
STEP II - ADIPONITRILE FROM FURFURAL



The second step in the new furfural to adiponitrile process is the hydrogenation of furan to tetrahydrofuran. This process may be carried out either

batchwise or continuously, in the presence of suitable catalysts (U. S. Patent 1,006,873). The yield of tetrahydrofuran is nearly theoretical.

STEP III - ADIPONITRILE FROM FURFURAL

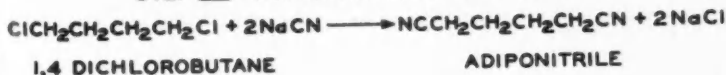


The third step involves reaction of tetrahydrofuran with hydrogen chloride to form 1, 4-dichlorobutane. This reaction may be carried out in a number of ways. If desired, tetrahydrofuran, hydrogen chloride, and water may be heated under pressure at elevated temperatures with or without catalytic materials. Hydrogen chloride may also be reacted with tetrahydrofuran at atmospheric pressure in the

presence of dehydrating agents such as zinc chloride or sulfuric acid, to give good yields of the dichloride (U. S. Patent 2,218,018).

Still a third method of carrying out this reaction involves the use of amine hydrochlorides as catalysts for the reaction. In all of the above methods of converting tetrahydrofuran to 1, 4-dichlorobutane, the yields of the dichloride are nearly theoretical.

STEP IV - ADIPONITRILE FROM FURFURAL



The fourth step involves the conversion of 1, 4-dichlorobutane to adiponitrile.

This is carried out by reaction of the 1, 4-dichloride with sodium cyanide.

nide in the presence of an appropriate solvent. The sodium chloride which is formed is insoluble in the reaction mixture; it is removed by filtration and the solvent and adiponitrile are then separated by fractional distillation. Yields on this step also are high.

The hydrogenation of adiponitrile to hexamethylene diamine, reaction of this with adipic acid, and further processing of the product to nylon, are carried out by means of established industrial practice. Adiponitrile can also be hydrolyzed to adipic acid, the other main intermediate in the process for nylon. However, the present installed facilities for the production of adipic acid from benzene, and not from furfural, will continue to be used.

Intermediates Available

A result of this new method of manufacture for nylon from furfural will be the availability of the three chemical intermediates—furan, tetrahydrofuran, and 1, 4-dichlorobutane—for other uses. Delta-chlorovaleronitrile can also be made available by a slight change in operating procedure. The Electrochemicals Department of the Du Pont Company has explored extensively other new synthetic organic chemicals derived from furfural.

Furfural is extremely attractive as a chemical raw material, as it possesses three highly reactive systems: an aldehyde group, conjugated double bonds, and an ether linkage.

To illustrate the versatility of furfural as a chemical intermediate, a simple example can be given: Examination of the first step in the new process for adiponitrile from furfural

shows that the carbon atom present in the side chain of furfural is removed as carbon monoxide. Other methods of operation may be used, however, which retain this carbon atom in the side chain as a methyl group, giving the compound 2-methyl furan; by tucking this carbon atom into the ring to give the 6-atom ring known as dihydropyran. These two compounds may be handled in much the same way as furan, yielding, as is indicated, pimelo nitrile and methyl adiponitrile respectively, in place of adiponitrile.

As a result of this exploratory work several other compounds based on furfural as a raw material have been made available for experimental purposes. Among these are 1, 4-butanediol, dihydropyran, tetrahydropyran, 1, 5-pentanediol, 1, 5-dichloropentane, 2-methyl furan, and 2-methyl tetrahydrofuran. The availability of additional compounds derived from furfural will be announced as this work proceeds.

Although these new furfural chemicals have been subjected to only preliminary evaluation, a number of applications can be mentioned.

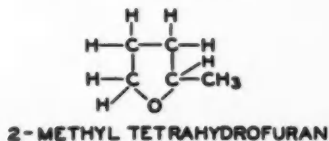
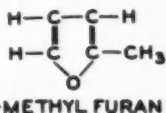
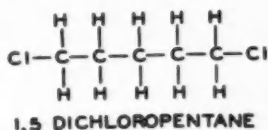
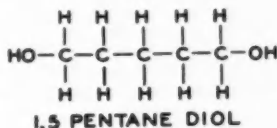
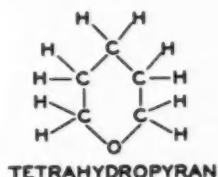
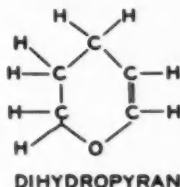
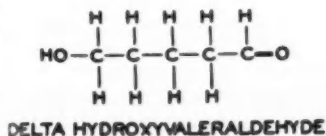
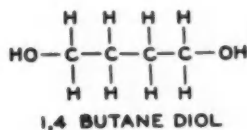
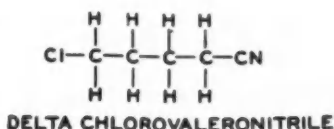
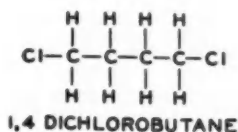
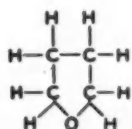
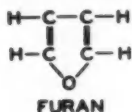
Tetrahydrofuran and tetrahydropyran are extremely active solvents for a wide variety of natural and synthetic products. For example, both vinyl chloride and vinylidene chloride type resins are highly soluble in either of these materials, while the moderate boiling points of the compounds (66° and 88° C., respectively) make their use as film-casting solvents for chloro-vinyl resins attractive.

Furan, methyl furan, tetrahydrofuran, and dihydropyran may be polymerized under a variety of conditions

sent in to yield polymers with a wide range of properties.

The greatest potential use of these compounds is, however, as chemical

NEW COMPOUNDS FROM FURFURAL



intermediates for the preparation of 4 and 5 carbon atom chains with a wide variety of reactive groups at each end. These compounds appear promising for the synthesis of pharmaceuticals, vitamins, plasticizers, and condensation products.

Promise of Furan Chemistry

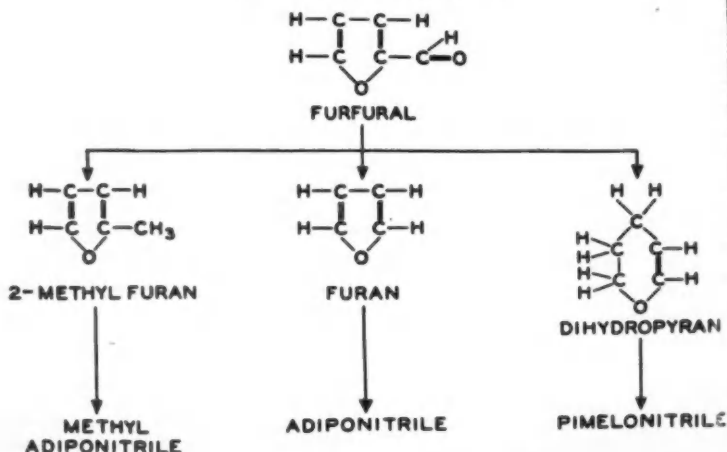
In 1939, four years after the work which has just been described was begun, Dr. F. N. Peters, in an article entitled "Industrial Uses of Furan," closed his remarks with this paragraph:

"Two great factors militate against the fruition of many of these projects—price, and lack of adequate research. Of these, the economic factor is of least importance, for, with sufficient volume, furfural can be made at an unbelievably low cost. Research is increasing. A prominent German chemist said recently that, if he had his way, he and his entire staff would

spend all their time in the field of furan chemistry. An equally prominent American chemist has predicted that, within twenty-five years, furan chemistry will be as well established industrially as benzene chemistry. Although this may seem an exaggeration, it is perhaps closer than many of us realize."

The field of furan chemistry which Dr. Peters so enthusiastically recommended in this paragraph has now been opened up. We believe, with Dr. Peters, that this field of chemistry will show as many outstanding results in the next decade as did the field of benzene chemistry or the field of lower aliphatic chemicals when these were first intensively evaluated. This development by Du Pont, which ties together the American farmer and the American chemical manufacturer in the production of nylon, is only one of many such coming achievements.

VERSATILITY OF FURFURAL



Pilot Plant Operation Shows Hydrochloric Acid Process Practical, Although Costly

Alumina From Clay

► THE DREAM of making shiny aluminum metal from a clay bank is coming true.

For nearly four years a pilot plant at the National Bureau of Standards has been producing from kaolin clay a raw material which is the practical equivalent of bauxite, hitherto the only usable ore of aluminum.

Dr. James I. Hoffman, government chemist, has been given the Hillebrand prize of the Chemical Society of Washington, D. C. as evidence that his colleagues consider his process a major chemical achievement.

There is now no practical limit to the amount of aluminum for a modern world that can be produced. Literally billions upon billions of tons of clay suitable for use in the Hoffman process underlie the southern states alone. It is the same kind of white or cream clay that is used in coating paper and some ceramic materials.

Only about six years' supply of bauxite exists in the country, according to a wartime estimate. The hurry-up development of the new process was begun as a hedge against the possibility that submarine warfare would cut us off from the British and Dutch Guiana bauxite upon which the U. S. is largely dependent.

The primary barrier today to the use of clay in aluminum production is cost. To produce clay of the needed purity by the Hoffman process costs about twice as much as high-grade bauxite under present conditions.

This important development is reported in a paper in the Journal of Research of the National Bureau of Standards for December 1946: "Development of a Hydrochloric Acid Process for the Production of Alumina from Clay" by James I. Hoffman, Robert T. Leslie, Harold J. Caul, Lewis Jesse Clark, and John Drake Hoffman. This article is available as Bureau of Standards Research Paper RP1756 from the Superintendent of Documents, Washington, D. C. for a remittance of 15 cents.

The process is described in nine steps, each of which necessitated considerable experimentation and development by the Bureau of Standards group, or by other and earlier work upon similar processes. The method is as follows:

1. Roasting clay at about 700 degrees Centigrade.
2. Digesting the roasted product with dilute hydrochloric acid.
3. Filtering to separate the insoluble siliceous matter from the solution containing the aluminum and soluble impurities, such as iron and alkali salts.
4. Concentrating the solution.
5. Precipitating the aluminum as the hydrated chloride from the concentrated solution by adding hydrochloric acid gas.
6. Removing the crystals of hydrated aluminum chloride.
7. Washing the crystals to remove adhering impurities.

8. Calcining the hydrated chloride to obtain alumina.

9. Recovering the hydrochloric acid from the waste products at the end of the process.

Since it was developed as a government research, any patents will be available to the public and anyone will have a right to use the process.

The process does not involve new and mysterious reactions, the paper points out. The basic reactions of this process, as well as other acid processes for the extraction of alumina from clay, had been used and studied at the National Bureau of Standards in the analysis of bauxite, high-alumina refractories, aluminum metal, miscellaneous ceramic materials, and in the redetermination of the atomic weight of aluminum.

The alumina (Al_2O_3) produced is the starting point in the production of metallic aluminum by electrolysis, which is the conventional method. In this respect the alumina from the process is the counterpart of bauxite as it is mined and prepared. The alumina of the Hoffman process is extremely finely divided, whereas the bauxite is granulated in form. A finely divided state may be a disadvantage in the reduction to metallic aluminum, because of dusting.

From the pilot plant at the Bureau of Standards, which is being improved through further work in details and economy, it is estimated that alumina can be produced for about \$60 per ton with coal used as fuel, while bauxite costs about \$30 per ton under present conditions.

Purifying Uranium

The Hillebrand prize for 1946 was given Dr. Hoffman not alone for his alumina process, but for a chemical contribution to the atomic bomb: "The concept and demonstration of the use of ether in the removing of impurities from crude uranium."

Details of the uranium work have not been freely released, but, as is often the case, some of the basic principles of the work can be found in the chemical literature of past years. Dr. Hoffman, in accepting the award, said in part:

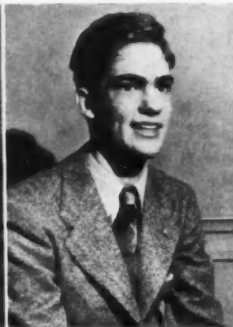
"It is a coincidence that the Hillebrand award should come to me almost exactly 25 years after Dr. Hillebrand himself asked me to separate uranium from other elements by the use of ether. Dr. Hillebrand had the germ of the present application of ether extraction of uranyl nitrate in U. S. Geological Survey Bulletin 78, back in 1891. Repeated application of ether extractions of uranyl nitrate for analytical purifications in our work during the early 1930's laid the foundation for the more rigid requirements that had to be met in 1940 and through the following years. It is a case where analytical procedure so highly regarded by Dr. Hillebrand, furnished the background for a useful industrial process. The story is similar in the work on the extraction of alumina from clay, but details are not necessary. Both cases furnish strong arguments for scientific research, even if that research does not have an immediate and definite end in view."

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CHEMISTS OF THE FUTURE

Within the limits of the accuracy of prediction—humans being less guessable than molecules—the Sixth Annual Science Talent Search for the Westinghouse Science Scholarships concluded in March has picked some of the young scientists who will do chemical research of importance in the future. Ten of the 40 young scientists who participated in the Science Talent Institute chose chemical subjects for their projects and essays. **CHEMISTRY** on the following pages presents these essays because of their intrinsic interest and their inspiration to all who are young in scientific spirit.



► *YOUNG CHEMISTS whose interests are described in the following essays are, left to right, Emrick, Gordon, Gregory, Haugh; House, Inman, Kopple, Mc Leish; Ren-nagel, Wilt. Some of them appear again in the S.T.S. Hobby Show pictures on the back cover and in the "memory book" shots of the Sixth Science Talent Search, on the inside back cover.*



Carnotite and Radioactivity

by DONALD DAY EMRICK, 17.

Waynesfield High School, Waynesfield, Ohio.

► THROUGHOUT the past six years, my interest in science, particularly chemistry, has grown with my increased study and experimentation in this vast field of human endeavor. Although I have conducted several investigations concerning the substitution of the element selenium for the sulphur in several organic sulphur compounds, particularly the simple thiols, and have made a few attempts to synthesize some of the simpler carbohydrates, I chose, instead, a project in another field of chemistry, inorganic chemistry, for the writing of this paper.

Although I first became interested in carnotite and uranium during my Sophomore year in school, it was not until this last summer that I decided to make a more intensive and complete study of the mineral and its constituents. Then, the object of this study was to be the extraction, separation, and study of the constituents of the radioactive mineral carnotite. I was motivated to conduct this project by my extreme interest in radioactivity and the radioactive elements; in addition, there was my desire to obtain compounds of uranium and vanadium for future laboratory study.

Pure carnotite, itself, is a brittle, yellow, radioactive mineral whose chemical composition is expressed by the formula $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$. It is found deposited in some of the sandstones of Utah and Colorado. However, a preliminary analysis of the carnotite I used in my investigations

showed that it contained only 14 per cent of pure $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$, despite the fact that it was of good commercial grade. The main impurity (some 86 per cent of the whole ore) was found to be sandstone, which in turn contained considerable amounts of iron and some calcium. Needless to say, the project was made more difficult by the comparatively large amount of these impurities.

After studying about the various properties and solubilities of the compounds of uranium, vanadium, lead, and radium, not to mention iron and calcium, I conducted several preliminary trial extractions. As a result of these trials and many costly errors, I worked out the following procedure for the extraction and separation of the constituents of carnotite. This procedure, which I will next describe, is not too complicated, is very economical, and will work well for low grades of the mineral.

The carnotite is crushed and powdered. The resulting powder is mixed with two to four times its volume (depending upon the mineral's purity) of sodium carbonate crystals; water is added and the mixture is boiled for one hour with occasional stirring and adding more water as necessary. After this boiling, the mixture is filtered, and the residue is washed. The residue consists largely of silica (sand), iron oxide, calcium carbonate, and contains smaller amounts of barium-radium and lead



► WHEN DR. L. F. SMALL, head chemist of the National Institute of Health of the U. S. Public Health Service, talked to the STSers, he brought along several complete outfits for opium smoking that had been seized in the government's anti-narcotic work. New organic chemicals promise to provide medical substitutes for such habit forming drugs.

(radioactive) carbonates; the filtrate contains soluble sodium uranate and vanadates. Twenty per cent (by volume) sulphuric acid is carefully added with constant vigorous stirring until the mixture is definitely acid to litmus.

The next step is the most crucial point of the whole procedure. Add a few extra drops or a few ccs (depending upon the quantity and purity of the mineral used) of dilute sulphuric

acid, then add solid ammonium chloride to the mixture, stir vigorously, and then slowly apply heat. A brownish or brownish orange (not yellow or yellowish) precipitate should form as the mixture is heated; if, instead, the precipitate is yellow or has too much of a definite yellowish tinge, remove the mixture from the flame, and add slowly, with vigorous stirring, small amounts of dilute sulphuric acid until the precipitate darkens to brownish

orange or brown, then reapply heat. After the mixture has boiled for a few minutes the precipitation is complete. This vanadium precipitate is separated from the clear liquid, which still contains the uranium in solution, by decantation or filtration. When this precipitate is washed, dried, and ignited, yellowish red vanadium pentoxide, V_2O_5 is produced. The vanadium pentoxide may then be dissolved in hydrochloric acid to yield vanadium chloride solution.

After the vanadium has been precipitated, leaving the uranium still in solution, strong sodium hydroxide solution is added to the clear solution. Insoluble yellow sodium diuranate will be precipitated. This yellow precipitate is then filtered off, washed, and then dissolved in dilute sulphuric acid. The uranium is reprecipitated by the addition of ammonium hydroxide. The resulting precipitated ammonium diuranate may then be washed, dried, and ignited to yield yellow uranium trioxide, UO_3 . Part of this uranium trioxide may be dissolved in dilute nitric acid to yield uranyl nitrate solution. Another part of the trioxide may be reduced and dissolved by treatment with dilute sulphuric acid and sodium amalgam to produce sodium uranous sulphate.

Back to the sandy carnotite residue, freed of most of its uranium and vanadium. The residue, which contains traces of radioactive lead and radium-barium carbonates, is treated with a slight excess of hot dilute hydrochloric acid. The calcium, radium-barium, lead, and some iron will go into solution as soluble chlorides which may be filtered off and collected. Freshly prepared ammonium acid sulphide is

added to the chloride solution, and the resulting mixture is allowed to stand two to three hours. A small quantity of a dark brown precipitate will have settled out. This precipitate is filtered off, saving the filtrate which still contains calcium and traces of barium-radium. The brownish precipitate is washed first with water, then with dilute sulphuric acid, and twice again with water; the washings may be discarded. The small quantity of brownish black residue remaining on the filter paper is essentially lead (isotope 206) sulphide made radioactive by traces of radioactive lead isotope 210 and polonium (isotope 210).

After the lead has been removed, the filtrate, which contains calcium and barium-radium still in solution, is treated with sodium bisulphate solution and allowed to stand for several hours. White, crystalline calcium-barium-radium sulphate (Ca , Ba , $RaSO_4$) will be found deposited. These insoluble crystals may be broken up, washed several times, and dried.

In actual practice the above procedure yielded some 15.2 grams vanadium pentoxide, 44.2 grams sodium diuranate (equivalent to 39.86 grams of uranium trioxide), .29 grams radioactive lead sulphide, and 1.82 grams calcium-barium-radium sulphate from 500 grams of 14 per cent pure carnotite. I determined the atomic weight of the uranium (by ratio of uranium in its oxide as compared with its ferrocyanide) to be 212. A determination of the atomic weight equivalent of the calcium-barium-radium part of the calcium-barium-radium sulphate gave approximately 66, thus indicating



► **PRESIDENT HARRY S. TRUMAN** received the winners of the *Sixth Annual Science Talent Search* at his White House office and the next evening he dropped in for a few minutes to see the project exhibits displayed at the Hotel Statler (as shown on the back cover). **BOTTOM:** The two top winners are congratulated at the close of the awards dinner. Left to right, Dr. Harlow Shapley, chairman of the judges board, Martin Karplus of Newtonville, Mass. and Rada Demerec of Huntington, N. Y., top boy and girl \$2,400 Westinghouse scholarship winners, Dr. Vannevar Bush, who delivered the principal address, and Watson Davis, director of Science Service.



that the latter sulphate was essentially calcium sulphate accompanied by very small quantities of barium and radium.

Tests for radioactivity in the above prepared carnotite constituents, as well as in a sample of thorium dioxide, were made, using Becquerel's photographic plate method. Judging from the intensity of the effect of each of the above substances on strips of photographic film, I decided that uranium and radio-lead showed the most intense effect on the film, next in intensity was the thorium dioxide sample, followed by calcium-barium-

radium sulphate, which, surprising as it may seem, showed only moderate radioactivity. In view of this latter fact, I have since come to the sorry conclusion that I lost most of the radium somewhere along the extraction procedure despite my careful precautions. In the near future I hope to discover this error by making radioactivity tests of each of the products resulting from each step of the procedure.

My project is not complete and before it is I hope to have isolated the vanadium, uranium and radio-lead as the free metals.

Indole

by MILTON PAUL GORDON, 16
St. Paul Central High School, St. Paul, Minn.

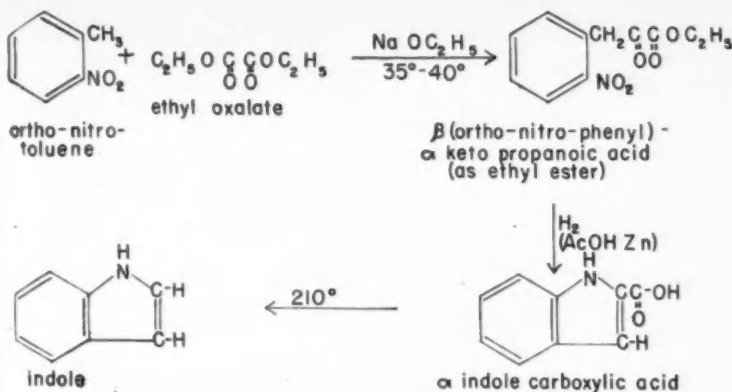
► IN RECENT YEARS indole and its derivatives have assumed an increasing importance in modern chemistry. The beta indole alkanolic acids have been found to possess great growth promoting activity and have been the subject of an enormous amount of research. Such so called plant hormones are destined to play an important role in the agriculture of tomorrow.¹

My introduction to this interesting class of heterocyclic compounds was the synthesis of indigo blue by fusing phenylglycine-ortho-carboxylic acid with sodium hydroxide and oxidizing the resulting indoxyl with ferric chloride and hydrochloric acid.²⁻³

The production of indole by the method of Arnold Reissert has been recommended by Shorygin and Polyakova after a thorough investigation.⁴⁻⁵⁻⁶ Reissert was studying the ac-

tivating influence of negative substituents other than the carbonyl group in promoting Claissen-like condensations.⁷ Reissert discovered that one mole of ortho-nitro toluene condenses with one mole of ethyl oxalate in the presence of two moles of sodium ethoxide. The product, beta ortho-nitrophenyl alpha keto propanoic acid, is the starting material for the synthesis which is shown in the accompanying diagram.

All apparatus and materials used must be kept scrupulously dry. The ethyl oxalate was dried for one hour over P_2O_5 and then distilled from a Claissen flask at about 15 m.m. B.P. 78°. 180 c.c.'s of alcohol was dried by refluxing with 4% of its weight of sodium (9 gm.) The equilibrium $C_2H_5ONa + H_2O \rightleftharpoons NaOH + C_2H_5OH$ is driven to the right by the excess



sodium ethoxide. The anhydrous alcohol was distilled into a 250 c.c. filtering flask with a calcium chloride tube as protection from atmospheric moisture. The first five portions of 5 c.c.'s each were used to rinse the flask.⁸ 92 gm. were collected, and 4.6 gm. of clean sodium was dissolved in the alcohol. After cooling 14.6 gm. of ethyl oxalate and 13.7 gm. of ortho-nitro toluene (B.P. 110 — 112 20 m.m.) were added. The flask was kept at 35 to 40 for 72 hours by a 10 w. light bulb immersed in a sand bath. The contents were then a deep dark red. 18.7 gm. of HCl in 300 c.c.'s of water were added, the solution saturated with salt, and extracted with ether until it showed only a faint coloration with NaOH. The ether was then extracted with 10% NaOH until the alkali took on no more color. Upon the acidification of the NaOH the free acid was precipitated as a fine yellow powder. Yield 10.3 gm. 50% M.P. 116—121.⁹

Five gm. of the beta ortho-nitro-phenyl alpha keto propanoic acid was

reduced with a boiling mixture of 25 c.c.'s of glacial acetic acid and 100 c.c.'s of water until it no longer gave a red color with NaOH. The acetic acid was neutralized to destroy its solvent properties, and the alpha indole carboxylic acid extracted with five 100 c.c. portions of ether.¹⁰ The ethereal extracts were placed in the 500 c.c. separatory funnel mounted so that it dripped into a 200 c.c. distilling flask placed in a warm sand bath. The ether was distilled, and the residue heated with a free flame until it frothed and distilled. A white crystalline mass of indole collected in the receiver. Yield 1.3 gm. 41.5% M.P. upon several recrystallizations 52°.

In the future I intend to try to improve the yield in the above process and then synthesize beta indole alpha acetic acid from N indole magnesium iodide and chloroacetonitrile.¹¹ I also intend to synthesize alpha naphthalene acetic acid, which also has powerful growth promoting properties, from alpha chloromethyl naphthalene by

means of the nitrile or carbonation of the Grignard reagent.¹²

References

- ¹Plant Growth Regulators. United States Department of Agriculture Miscellaneous Publications No. 495.
²Organic Chemistry, Lucas, P. 609.
³Richter's Organic Chemistry, Smith. Vol. 2 P. 468 Par. 5.
⁴Beilstein's Handbuch Der Organischen Chemie, Vierte Auflage Vol. 20 P. 304-305.
⁵Organic Synthesis Vol. 23, P. 42. The excessive price of metallic potassium made this method prohibitive.
⁶Shorygin and Polyakova. Chemical Abstracts. Vol. 36, P. 3902, 1942.
⁷Arnold Reissert, Berichte. Vol. 30 P. 1045, 1897.

⁸Laboratory Technique in Organic Chemistry, Morton, P. 14.

⁹The presence of a small amount of the para nitro compound also aids in producing the wide range in the melting point. It is pure enough for the next step as the para nitro compound cannot cyclize.

¹⁰The ether should be shaken with a dilute solution of FeSO_4 and HCl to destroy the explosive peroxides. The presence of peroxides may be tested for by means of a solution of FeSO_4 and KCNS . The peroxides oxidize the Fe^{2+} to the Fe^{3+} ion which gives a blood red color with the CNS^- ion. Organic Chemistry, Karrer, P. 106; Experiments in Organic Chemistry, Fieser P. 362.

¹¹P. Majima and T. Hoshino. Berichte. Vol. 58, P. 2042, 1925.

¹²Organic Reactions, Vol. 1, P. 70.

Molecular Weight Determination

by CLARENCE LESLIE GREGORY, JR., 16.
Brunswick High School, Greenwich, Conn.

► WHEN THE ORGANIC chemist is undertaking a synthesis in which a product is formed of uncertain identity, an easy and limiting method of determining the size and structure of its molecule is necessary. A molecular weight determination can quickly cut the structural possibilities down to a few, which can then be checked by more exhaustive tests, as well as permitting the calculation in many cases of the specific number of atoms of each element present. Consequently, I undertook the study of this phase of physical chemistry as an aid to my future work in attempting original preparations and syntheses. In addition, the mathematical and physical aspects of this field have interested me greatly, and I have been quite anxious to increase my knowledge of this subject.

Methods of Determination

Several methods of molecular weight determination have been de-

veloped which depend on various physical-chemical laws.

1. In the Vapor Density Method the weight of an unknown vapor can be compared to an equal volume of a known, and the molecular weights are thus in direct proportion. Although this method is quite simple and accurate, it is quite difficult to measure, without specially-constructed and elaborate equipment, vapors of substances which boil at high temperatures or tend to associate or dissociate.

2. The Lowering of the Vapor Pressure Method is based on Raoult's Law stating that the fraction by which the vapor pressure of a solvent is lowered when a non-volatile substance is dissolved in it is equal to the mole fraction of the solute. In this way the difference in vapor pressure may be measured directly, as with Menzies' apparatus (1910). However, this lowering of the vapor pressure also causes

a rise in the boiling point, and this fact permits the use of a method involving the measurement of the differences of temperature instead of pressure. After a survey of the various methods this one seemed to me to be the most suitable for me to study as it was easily applicable to non-volatile organic compounds. It seems to be one which has been generally found of most value in analysis. The lowering of the freezing point, which also occurs when substances are dissolved in given solvents, can likewise be measured for the same purpose.

3. The osmotic pressure of solutions of proteins can be used to determine their molecular weights.

4. The molecular weights of organic acids may be determined by preparing their silver salts and calculating the percentage of silver therein contained.

Elevation of Boiling Point

According to Raoult's Law,

$$\frac{P - p}{P} = \frac{n}{N + n}$$

in which $P - p$ equals the lowering of the vapor pressure in the given solution; P , the normal vapor pressure of the solvent; n , the number of molecules in the solute; and $N + n$, the number of molecules in the solvent. The number of moles may be substituted in the formula for number of molecules so that it now reads

$$\frac{P - p}{P} = \frac{\frac{w}{M}}{\frac{W}{M} + \frac{w}{m}} \quad \text{or}$$

$$\frac{P - p}{P} = \frac{wM}{Wm + wM}$$

The term wM is usually dropped from the denominator since Wm is so large in comparison.

The application of this law to the elevation of the boiling point of a solution lies in the fact that since the vapor pressure is lowered in proportion to the number of moles of solute, the boiling point will be raised proportionately also. Therefore, the formula,

$$T_1 - T = \frac{Kw}{Wm}$$

can be deduced, in which K is a constant representing the boiling point elevation of a mole of solvent for each mole of solute at atmospheric pressure, the value herein for P . Each quantity in the above equation can be readily evaluated when m is being sought except $T_1 - T$ which must be determined with special apparatus, which I have been studying.

Construction of Apparatus

The first method to be used was that of Beckmann (1888). However, since it is subject to superheating, I decided to turn my attention to the Landsberger apparatus (1898) first. This involves the boiling of the given solvent in a separate flask and passing it through a tube to the bottom of a second vessel containing the same solvent. The vapor gives up its heat of vaporization to the second volume of solvent until this in turn boils. The boiling point is then measured, and a known weight of solute added to the latter vessel. Although the vapor of the solvent coming from the first

flask is able to raise the solution in the second to its boiling point, there theoretically is no danger of superheating since the vapor will no longer give up its heat of vaporization.

I undertook the construction of apparatus based on this principle and finally succeeded in obtaining one which gave fair results. Vapor is supplied from an Erlenmeyer flask and conducted through glass tubing to the bottom of a test tube containing more solvent and situated in the neck of a distilling flask. When this solvent boils, the temperature is read on a thermometer. The vapor from the test tube passes out through an opening near the top, which I blew in the test tube, and into the distilling flask, thereby forming a vapor jacket preventing the loss of part of the heat by radiation.

With carbon tetrachloride as a solvent and chloral hydrate as a solute I obtained the following results:

$$T = 76.84^{\circ}$$

$$T_1 = 77.24^{\circ}$$

$$T_1 - T = .40^{\circ}$$

My thermometer was graduated in $\frac{1}{8}^{\circ}$, but it was easily possible to estimate fiftieths of a degree with the aid of a lens. However, the apparatus was unable to keep a constant temperature, and it was necessary to take an average of several readings. Also, I had no means of making corrections for barometric pressure. As I measured approximately 175 grams of carbon tetrachloride in the test tube after obtaining the boiling point of the solution, and had added .251 grams of chloral hydrate, I made my calculations as follows (boiling point con-

stant for carbon tetrachloride is 5000):

$$m = \frac{(5000) (.251) 1255}{(.4) (175) 7} = 179.3$$

Since the molecular weight of chloral hydrate is 165.4, I made an error of + 8.4% which was probably caused mainly by the fact that some of the solution splashed out through the hole in the test tube, although it was above the level of the solution when quiet.

I am now undertaking to correct some of the errors by improving my apparatus. I plan to provide a vapor jacket which will keep the heat more uniform as well as to alter the shape of the test tube to prevent loss of solution by splashing. In this way I hope to obtain results accurate to within 5%.

I have obtained apparatus for the Beckmann method as well as a differential thermometer which I have not been able yet to set. I expect to study the Cottrell Method (1919), but the expense of the pump involved may prevent me from using it. I have attempted to construct apparatus based on Menzies' (1910), but I have been unable to do so yet.

The Vapor Density Methods have interested me, and I plan to construct apparatus for at least one of them since they are usually accurate if the compound vaporizes readily.

When I have mastered these techniques and principles, I hope to use them when I turn my efforts to a study of the preparation of aromatic nitro and amino compounds. My particular interest is in aromatic aliphatic ethers containing these groups.

Extraction of Uranium

by EUGENE FREDERICK HAUGH, 17.
Reedsburg High School, Reedsburg, Wis.

► ONE OF MY FRIENDS was constructing a Geiger counter and I told him that when he had it finished, he could test some carnotite that I had with it. But I thought I would see if I couldn't obtain a uranium salt or metallic uranium from it so that he would have stronger radiation to work with.

The first thing I did was try to find out how to extract a salt. I looked through all the books that I could find. The nearest method that I found was the method used for tungsten, a metal chemically related to uranium. I intended to utilize the same reaction because the oxidation state of uranium in carnotite is the same as for tungsten in its ore, calcium tungstate. To be able to judge the reaction, I first tried it with calcium tungstate and did get the desired results.

When I tried it with carnotite, however, it didn't work. Knowing that the uranium of the compound was it was a fairly active metal, it seemed present in its oxide form and that that treatment with hot acid would dissolve it in the form of the salt of the acid used. Now the only difficulty would be that along with the uranium salt would be salts of potassium and vanadium.

I made three solutions, one in hydrochloric acid, one in nitric, and one in sulfuric acid. It was apparent by the coloration produced that something had dissolved in each case. The nitric and sulfuric solutions were brown; so was the hydrochloric until

I heated it. Then it turned an olive green. I didn't know why this should happen unless something additional had dissolved or something else had happened. I repeated the experiment and filtered the brown solution that formed first. Now I heated the separated solution and found that it turned green. Hence some new reaction had taken place.

I searched for a chemical test for uranium but could find no simple one. I tested for it by placing the solute on photographic film. When I developed it, there was an image; hence, I had uranium. To see if the solution contained vanadium, I gave it a test that I was able to find; it did contain it.

To separate the uranium, I looked through my handbook to see what I could find regarding the solubilities of corresponding vanadium and uranium compounds. I found that there were several different series of uranium compounds—the trivalent, tetravalent, pentavalent, and the uranyl, UO_2^{++} . And all the chlorides were soluble! I found that uranyl chloride was yellow, and since vanadium chloride is green, it was just possible that this is what was in solution. As for what caused the brown color, it may have been due to uranium trichloride which is brown; this substance may have later changed to the uranyl because of the heat. But as for finding a means of separation, I could find nothing of value insofar as a possible method was concerned.

Still, however, I knew that sodium uranate was insoluble because the first method was supposed to work if it were soluble; and since it failed, it must be insoluble. But what about sodium vanadate? I looked it up and found that it was soluble. Here then, was a possible means of separation providing they could be made at the same time.

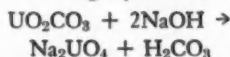
To do this, I went back to tungsten again. I found that sodium tungstate was made by the action of hot sodium hydroxide on tungsten oxide. Then I had to make the oxide. I figured that I could do this by heating the hydroxide of uranium and vanadium. This I thought I could make by adding sodium hydroxide to the acid solution; and hoping the hydroxide to be insoluble, I could separate it from some of the rest by filtration.*

Unfortunately, the method was a "flop." I did obtain a precipitate and it did contain uranium and vanadium, but I could not make the oxide from it. At least none of the precipitate would dissolve in the sodium hydroxide.

Now I had to make the oxide a different way. So, remembering that lime is made by heating the carbonate, I thought I might be able to get the oxide by heating the carbonate. I took my acid solution and added sodium carbonate and saw a precipitate form. To find if the uranium had precipitated, I tested the solution first for vanadium and found that it had precipitated. Then I added sodium

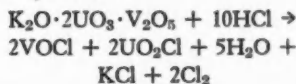
hydroxide and saw an unexpected reddish precipitate form. I filtered, washed, and dried it. Here then, must be a precipitate of a hydroxide of some sort of uranium (I thought).

But I found that uranyl carbonate was supposed to be insoluble. This would mean that any uranyl chloride which had been in solution had already been precipitated and therefore, I could not possibly have uranyl hydroxide. Then I noticed something else. Uranyl carbonate was soluble in excess sodium carbonate; and therefore, it might be possible that that's what I did have. I was so mixed up that I thought maybe I might even have a precipitate of sodium uranate. Just for a nutty idea, I tested it for sodium and to my astonishment, it did contain it. Therefore, I must have sodium uranate. It might have come from the uranyl carbonate (which I guessed I had had before) by the following equation:



I had to suppose that I had the sodium uranate because it contained sodium and uranium and that is the only compound of that type I know.

I finally arrived at the following equation for the reaction of carnotite and hydrochloric acid:



The reasoning I used to obtain the above result would take too much space to explain. Actually, when I dissolved the carnotite, small bubbles of a gas were formed; apparently this

*I was wrong in my reasoning because I overlooked the fact that uranium and vanadium were already present as oxides in the ore and all this treatment was unnecessary. However, it is this error that saved me later on.

was the chlorine. I have no quantitative analysis to back up this equation, however.

This is all the further that I have carried the extraction of uranium. I intend to see if I cannot find a method

to separate the uranium from the sodium uranate. If I cannot, then I'll have to try it with the sulfuric acid or nitric acid solution. Maybe I can do it that way. The whole problem is a very interesting one.

The Barbiturates

by HERBERT OTIS HOUSE, 16.

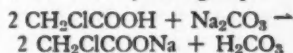
Willoughby Union High School, Willoughby, Ohio

► BIOCHEMISTRY holds for me a fascination above that of all other branches of chemistry. This interest is due to its infinite possibilities and its definite vital applications to the welfare of mankind. Biochemical discoveries and products constantly offer new hopes for the diseased victims and support progress in longevity. The unlimited realms such as chemotherapy, hormone study, nutritional problems and the mystery of viruses and life itself lie ahead of us awaiting the probing of some biochemist.

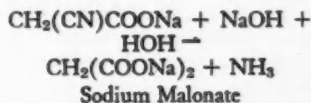
My foundation in chemistry was laid about five years ago when I set up a laboratory in our basement. This hobby soon became my chief interest and I built as complete a laboratory as possible and bought many books. About a year ago my interest was drawn to the biochemical phase of chemistry. To begin I purchased five white mice and bred enough for my experiments. One of my experiments was to inoculate mice with varying quantities of chloral hydrate to determine the normal dosage, the minimum lethal dosage, and duration of the effect. This experiment besides allowing me to learn laboratory technique kindled an interest in hypnotics

and sedative drugs and served as a prelude to experimenting with barbiturates.

I chose veronal as a representative of the many barbituric derivatives. Veronal is the diethyl derivative of barbituric acid and finds much use as an ingredient of sleeping pills. My starting product for the synthesis of veronal was mono-chloro-acetic acid. The first step in this synthesis was to neutralize the acid and replace the chlorine with a cyanide group;



The next step in the synthesis was the hydrolysis of the cyanide derivative with a solution of sodium hydroxide as follows:



To the sodium malonate thus prepared was added a soluble barium salt to precipitate the malonate as an insoluble barium malonate. This precipitate was washed repeatedly, then

treated with sulfuric acid and warmed with constant stirring. The free malonic acid was separated from the barium sulfate by filtration. The filtrate was evaporated and extracted with ether. The extract was evaporated and pure malonic acid was obtained. From this acid the ester was prepared by refluxing with absolute alcohol and sulfuric acid for about three hours. The water and excess alcohol were removed by fractional distillation and more alcohol and malonic acid were added. The refluxing continued for another two hours and the excess acid was neutralized with saturated

Na_2CO_3 solution and the ethereal layer was extracted.

The entire barbituric family belongs to the pyrimidine family which contains other compounds of interest to the biochemist. Pyrimidine, whose formula is heterocyclic in structure, is composed of four carbon atoms and two nitrogen atoms in the 1,3 positions. (See Fig. 1).

The barbiturates are formed by the reaction of an allyl malonic ester and urea as shown in Fig. 2.

The physiological effects of the barbiturates are entirely dependent upon the alkyl groups R and R' in the formula.

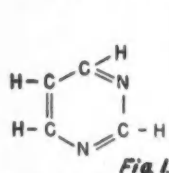


Fig. 1.

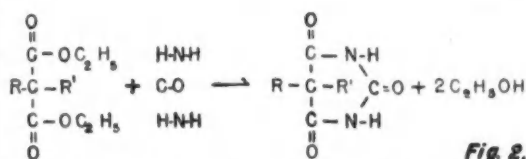


Fig. 2.

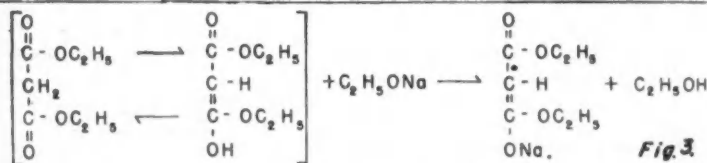


Fig. 3.

To continue with the preparation of veronal, it was time to replace the hydrogen atoms of the malonic ester with alkyl groups and in this case with ethyl groups. The success of this reaction was dependent on dryness for a maximum yield. The malonic ester was placed in a flask with absolute ethyl alcohol to which metallic sodium was also added, thus removing practically all of the water. Sodium ethoxide reacted with the ex-

cess malonic acid to form the sodium enolate of malonic acid.

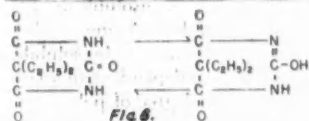
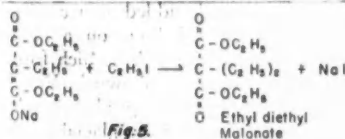
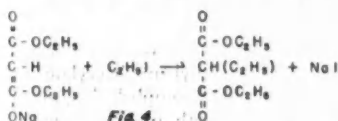
This reaction was due to the malonic ester being tautomeric and proceeds according to the equation in Fig. 3.

Ethyl iodide was next added, refluxing the mixture for two hours; next enough ethyl iodide was added to substitute ethyl groups for both sodiums which had already replaced the hydrogens, as shown in Fig. 4.

The product of this reaction reacted with more sodium ethoxide undergoing a tautomeric change to substitute a sodium atom for the other hydrogen, as indicated by Fig. 5.

The ethyl diethyl malonate formed was added to absolute ethyl alcohol and sodium ethoxide; then urea was added. The ethyl alcohol was distilled off and the content was held at a temperature of 110-115 C. while the sodium salt of veronal was distilled. The distillate was dissolved in water and sulfuric acid was added to liberate the veronal from its sodium salt. Then the veronal was recrystallized from water in a pure form.

The barbital salts form because of their tautomeric nature. The hydrogen migrates from the nitrogen in the keto form to attach itself to the oxygen forming the enol form. (Fig. 6).



I neutralized the pure veronal with sodium carbonate to form the soluble sodium salt, in order that the drug could be given hypodermically. As a starting point to determine the proper

dosage for the mice, I set up the following proportion:

Average weight of human in grams

Average weight of mice in grams

Human dosage*

Theoretical dosage

The result of the above proportion was 0.11 milligram. However from previous experiments I found that mice have, relative to their comparative weights, a higher tolerance for most drugs than the human. As a first trial I used dosages of 0.2 mg, and 0.6 mg but these were all too small as they had no noticeable effect on the mice. I increased the dosage to 1.0 mg and 1.5 mgs and both of these quantities showed mild signs of effect in seven to eight minutes. The animal appeared dazed and unsteady due to the barbital preventing the afferent impulses from reaching the sensory parts of the brain and dulling other nerve centers. The mice were relaxed in about twenty-five minutes. They could be aroused by strong light or sudden noise. The duration of the effects of the drug was about 2-3 hours. I continued to increase the dosage and found that 2.0 mgs, 2.5 mgs, and 3.0 mgs have effects similar to those of the previous dosages; differing only in the time it took the drug to take effect, the larger dose took effect in about twenty minutes. On increasing the dosages to 4.0 mgs and 6.0 mgs a general anesthesia, from which the animal could not be aroused, was the result. The mouse given 4.0 mgs recovered in two and one-half hours while the one given 6.0

*Textbook Materia Medica — "Blumgarten."

mgs required three and one-half hours to recover. I found the minimum lethal dosage to be 8 milligrams.

Due to my experience with veronal I plan to continue my experimentation with other derivatives about which less is known. The possibilities in anesthesia are shown by the wide

spread usage of sodium pentothal, a thiobarbituric acid derivative. I hope to use guinea pigs for these experiments as their size will simplify inoculation.

It is my desire to obtain a doctors degree and carry on research in the biochemical field some day.

Polymerization

by CHARLES GORDON INMAN, 17

Buffalo Bennett High School, Buffalo, N. Y.

► SINCE PERFORMING my first organic experiments in my laboratory three years ago, I have become increasingly interested in the phenomenon of polymerization. The challenging complexity of the reactions and the far-reaching industrial applications of this field have induced me to devote a large portion of my time to its investigation. Hence, for my research topic I have chosen the preparation and study of various representative polymers.

Among the first polymers which I synthesized were the alkyd resins. This is an important group of polyesters derived from dibasic acids and polyhydroxy alcohols. By warming a mixture of 2 g. of phthalic anhydride and 0.8 cc. of ethylene glycol just to the boiling point in the flame of a Bunsen burner for 15 minutes, a hard, red polymer was produced. This condensation product contains long chains of successive ethylene and phthalic acid residues joined by ester links, and the reaction may be represented as shown in Fig. 1.

Another alkyd resin, known as a Glyptal, was prepared according to

the above procedure by substituting 0.6 cc. of glycerol for the ethylene glycol, and adding 0.1 g. of sodium acetate to the mixture. A hard, brown resin resulted, which, because glycerol has three hydroxyl groups, is a cross-linked polymer. Alkyd resins are used in the preparation of synthetic enamels.

As a representative of the acrylic resins, polymethyl methacrylate was produced. To accomplish this, methyl methacrylate, with a small amount of benzoyl peroxide added as a catalyst, was heated for $\frac{1}{2}$ hour on a steam bath. The colorless solid which formed has the structure shown in Fig. 2. I have found that this product is soluble in acetone and in glacial acetic acid, although it is insoluble in 10% sodium hydroxide solution and in ethyl alcohol. However, the solubility of the polymer is dependent to a large extent upon the degree of polymerization. Because of its light weight and moulding properties, polymethyl methacrylate (Lucite) finds application in airplane windows, decorative fixtures, and in dentures.

While most synthetic elastomers

are extremely difficult to produce in a home laboratory, several of the thioplasts (reaction products of aliphatic dihalides and alkali polysulfides) may be synthesized with little difficulty. I prepared Thikol A by refluxing a solution of 6 g. of sulfur, 15 g. of hydrated sodium sulfide, and 50 cc. of water for 1 hour at 75° C. A yellowish, pliable solid was formed. The reaction involves the loss of sodium chloride and the linking of the ethylene and

polysulfide groups into long chains. The probable reaction is diagrammed in Fig. 3.

Thikols are resistant to hydrocarbons. Hence, they are employed in the manufacture of hoses and gaskets for the oil industry.

Another type of polymer of great industrial importance is the urea-formaldehyde resins. A methylol-urea molding powder was produced by heating 1.5 g. of urea, 2 cc. of for-

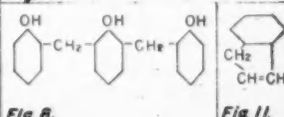
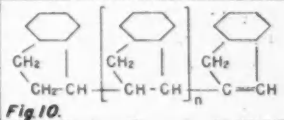
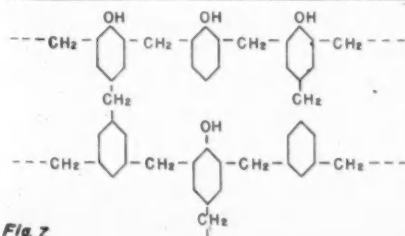
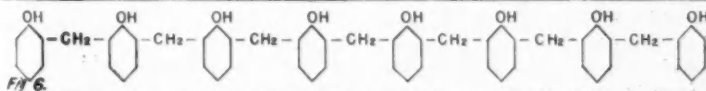
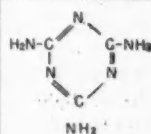
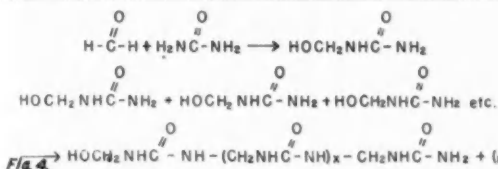
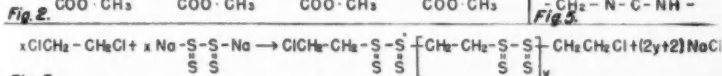
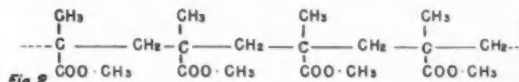
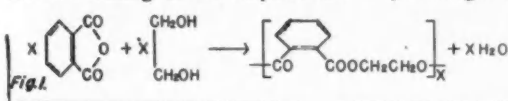


Fig. 11.

malin, and a small amount of boric acid on a steam bath for 30 minutes. A white powder—a lyophobic colloid—remained. It is believed that initially, the urea and the formaldehyde combine by addition to form hydroxymethylurea, which condenses with itself to form a polymer. These reactions are shown in the equations in Fig. 4.

Further reaction of the long polymeric chain with more formaldehyde is also involved. Some of the —NH— groups add to formaldehyde, forming



groups at points along the chain. If the powder is heated in a mold, these groups will react with free —NH— groups in adjacent chains to form a thermosetting plastic as shown in Fig. 5.

This three-dimensional structure is similar to that of the phenolic resins. Cabinets, tableware, and shatterproof electric light shades are made from urea-formaldehyde resins.

However, my experiments have been concerned principally with the phenol-formaldehyde resins. I obtained a simple phenolic resin from a mixture of 0.1 mole of phenol, 0.08 mole of formaldehyde, and 0.0008 mole of hydrochloric acid, a catalyst (calculated on the basis of hydrogen chloride gas). After heating for 2 hours on a steam bath, a viscous resin was formed which became a soft, transparent solid upon standing for a week. This resin probably consists of seven phenolic nuclei joined together by methylene bridges. The formula for this low polymer is given in Fig. 6.

This novolak is still fusible and I have found it to be soluble in acetone, in 10% sodium hydroxide solution, and in ethyl alcohol.

A higher molecular weight polymer was synthesized by heating 2 cc. of formalin and 0.8 g. of resorcinol, a substance having properties similar to phenol, on a steam bath for 15 minutes. An orange-red polymer which darkened over a period of several months resulted. Still another phenolic resin was made by heating 2.5 g. of phenol and 1.6 g. of para-formaldehyde until the phenol melted and dissolved the paraformaldehyde. Upon adding 0.1 g. of sodium hydroxide to bring about condensation, I found that a viscous, yellow resin formed which was soluble in acetone, in 10% sodium hydroxide solution, and in ethyl alcohol. A portion of this resin was heated over a free flame and a hard, red, infusible material resulted. This substance (Bakelite) proved to be insoluble in the three reagents which dissolved the initial yellow resin. The difference in properties of these two resins is due to the formation of cross-links during heating as shown in Fig. 7.

After standing for six weeks, the viscous resin also darkened and hardened to a lesser degree.

A number of low polymers of the phenol-formaldehyde type may also be prepared from formaldehyde and para-cresol, a member of the phenol group. Attempts to form 4,4'-dimethyl-2,2'-dioxo-diphenylmethane, a crystalline substance melting at 126°C ., were unsuccessful. It should be possible to prepare this substance by heating 0.1 mole of para-cresol, 0.009 mole of formalde-

hyde, and 0.0008 mole of hydrochloric acid. I did succeed, however, in forming the tri-nuclear compound by increasing the ratio of cresol to formaldehyde to 1:0.35 and heating with the same amount of hydrochloric acid for 4 hours. Melting point determinations showed that the main portion of my product melted at 190° C., while the pure compound should melt at 215° C. This substance has the structure diagrammed in Fig. 8.

Furthermore, in addition to the polymers already mentioned, I have also prepared several others. Included among these are an acetone-formaldehyde resin, a phenol-hexamethylene tetramine resin, and an acetaldehyde resin (hot, concentrated sodium hydroxide solution reaction).

At present, I am awaiting the arrival of chemicals necessary in the preparation of melamine-formaldehyde condensation products and polyindene. The difficulty in determining the structure of melamine polymers (melamine has the formula in

Fig. 9) is great because methylol groups, methylene bridges, ether linkages, and azomethine bridges may all or in part be present in the molecule. On the other hand, the structure of polyindene has been fairly well established as diagrammed in Fig. 10. Polyindene is polymerized from the monomer shown in Fig. 11, by the action of heat or light, and the addition reaction is accelerated in the presence of sulfuric acid or stannic chloride. Indene resins are useful as plasticisers for both natural and synthetic elastics while melamine resins are becoming keen competitors of urea-formaldehyde resins.

My experiments in polymerization, while elementary, are providing me with an understanding of the principles involved in this important branch of organic chemistry. I intend to continue my experimentation and I am earnestly anticipating the time when I shall be qualified to contribute materially to advances in plastic research.

Azo Compounds of Pyridine

by KENNETH DAVID KOPPLE, 16.
Cheltenham High School, Philadelphia, Pa.

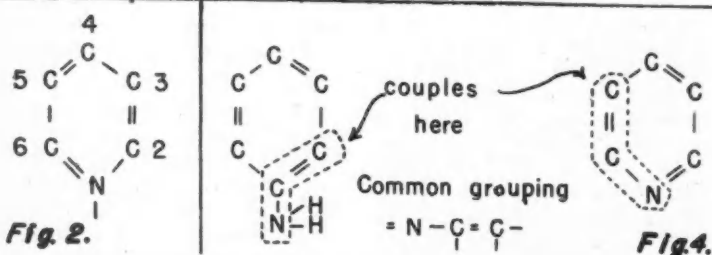
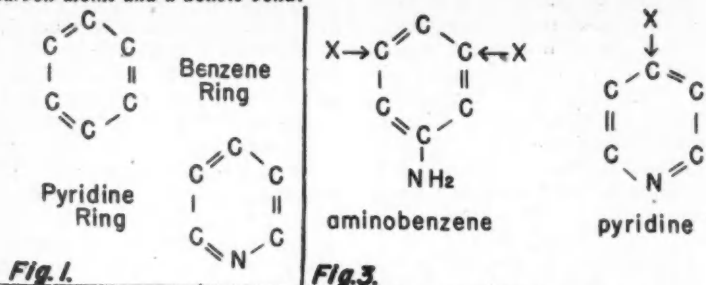
▶ SINCE ORGANIC CHEMISTRY aroused my interest at the beginning of my high school career, I have undertaken several simple projects in that field.

The first project, begun without any definite preparation, was an attempt at preparing silico-organic compounds such as the famous silicones. This was done by reacting the Grignard reagent—an alkyl magnesium

halide—and silicon tetrachloride. After getting results in agreement with information already acquired, I gave up the project because of very permanent and insoluble silicone gums formed on glassware and apparatus in contact with the reagents.

Toward the end of my work on the silicones, I conceived the idea of substituting calcium for the magnesium

► THE X POSITION, meta or equivalent, is separated from the nitrogen by two carbon atoms and a double bond.



in the Grignard reagent. Since both these elements are in group II-A in the periodic table, there was a chance that this substitution might work. Through various experiments tried, I found that calcium does not react with alkyl halides to give alkyl calcium halides.

My third project, work on the azo compounds of pyridine, gave some definite results which I shall attempt to describe.

Before undertaking any actual experimenting, I visited the library of the Benjamin Franklin Institute. Library research there in various reference books, including Beilstein's *Handbuch der Organischen Chemie* and *The Chemical Abstracts*, showed that syntheses of azo compounds of

pyridine were possible. Two basic methods were mentioned:

- (1) The reduction of nitropyridines—
 $2C_5H_4(N)NO_2 + 8H \rightarrow C_5H_4(N)NHC_6H_4N + 4H_2O$
- (2) Coupling of amino pyridines with diazonium compounds—
 $C_5H_4(N)NH_2 + C_6H_5N_2Cl \rightarrow C_5H_4(N)(NH_2)NNC_6H_5 + HCl$

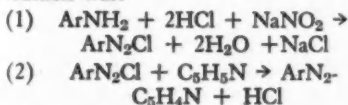
In the literature read, there was no mention of coupling diazonium compounds and unsubstituted pyridine or its methyl substitution products.

Aromatic diazonium chlorides ($C_6H_5N_2Cl$) react with tertiary aromatic amines ($C_6H_5(CH_3)_2N$) to give azo compounds of varying colors. Although pyridine is a tertiary aro-

matic amine, it is also a heterocyclic compound with nitrogen placed directly in the ring. This nitrogen atom places a high degree of restraint on the ring and renders it resistant to many substituents which attack regular benzene derivatives.

My research was to determine whether or not a diazonium compound would couple with pyridine in spite of the restraint on the heterocyclic ring and to find what effect, if any, positive (electron-releasing) substituents such as the methyl group, would have in reducing this restraint.

To experiment along this line, I planned to diazotize an aromatic amine and react it with a pyridine compound, observing the colors produced. The course of the hoped-for reaction was:



First attempts at coupling pyridine with a diazonium compound resulted in failure, which was at first mistakenly traced to imperfectly diazotized dinitroaniline. Later, it appeared that my methods did not allow the coupling reaction to proceed under favorable conditions. Alpha naphthylamine was tried and discarded before I discovered that the reason for failure lay in the coupling and not the diazotization reaction.

Sulfanilic acid, the only other available amine, was tried. Since this compound, when diazotized, falls out of solution, it was easy to tell when the diazotization reaction was complete.

The following method was evolved for the diazotization and coupling re-

actions: Sulfanilic acid (para aminobenzenesulfonic acid) is dissolved in a solution of potassium hydroxide and sodium nitrite and diazotized by addition of hydrochloric acid. The diazo compound formed is added to a solution of the pyridine homologue in sodium acetate. A pH of 5.6 is produced, right for the desired reaction. Coupling of one type or another is indicated by a change in color.

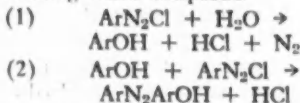
To run a typical experiment .45 gram of sulfanilic acid is dissolved in 12 c.c. of concentrated potassium hydroxide solution and .3 gram of sodium nitrite added. To this solution, cooled in an ice bath; concentrated hydrochloric acid is added, drop by drop. After the first few drops, the solution turns orange. When perhaps twenty drops are added, the solution is once again yellow and soon precipitates diazosulfanilic acid. The test tube containing the solution and precipitate is kept in the ice bath to prevent decomposition.

A solution of three c.c. of the pyridine derivative to be tested and five c.c. of the 3N sodium acetate solution is prepared and cooled in the ice bath.

For coupling, the contents of the two test tubes are mixed and agitated.

Although excesses of the pyridine homologues were mixed with the diazo compound, much of the precipitate of diazosulfanilic acid which was formed during diazotization remained undissolved for the first few hours at room temperature. After that time, or upon heating, the whole

mixture, of diazo compound and pyridine compounds became dark red-brown. Since control tests without the pyridine derivative showed that same characteristic, it was assumed that this color change is caused by decomposition of some of the diazo-sulfanilic acid to the phenol and its subsequent combination with the remaining diazo compound



This side reaction seems to indicate that the reaction between the diazo compound and the heterocycle, if any, is very slow.

On examining the reaction mixture within 30 to 60 minutes of its making, however, colors of entirely different hues showed up, varying with the various picolines, pyridines, lutidines, and collidines. Kodachrome transparencies of these colors were made and the results examined and compiled below.

TABLE ONE
Colors Given in Reaction of Diazo-sulfanilic Acid with Pyridine Homologues
(in order of increasing depth)

Yellows	
Control	(almost water white)
Pyridine	(3,5 dibromopyridine)
Beta-Picoline	(2,6 dibromopyridine)
Alpha-Picoline	
Oranges	
2,6 Lutidine	
Gamma-Picoline	
2,4,6 Collidine	
Red	
2,4 Lutidine	

(Those compounds shown in parentheses were solids tested in small quantities not proportional to those of the liquids tested.)

Examination of some of the colored solutions produced showed that they have indicating properties, changing color with varying pH. The most extensively studied reaction product, that formed by the reaction of 2,4 lutidine and diazosulfanilic acid, changes from orange to red at a pH of about 5-6 while the color formed with 2,4,6 collidine shows the same change at pH 7-8.

Lack of time, skill, and equipment prohibited any but the most rudimentary tests concerning the structure of this set of colors.

Since no other courses for the reaction could be plotted, except for the decomposition reaction already mentioned and the diazo coupling hoped for, it was thought that these latter colors were due to coupling of the pyridine compounds with the diazosulfanilic acid.

Results outlined in the above table show that the methyl group substituted in pyridine ring in the picolines, lutidines, and collidines exerts some effect on the color of the reaction product. Closer inspection reveals that this group has its greatest color-deepening effect when in the 2 or 4 positions or both (figure 2). Since the methyl group does not have much effect on color itself, the differences in color depth, may be explained as results of increased reaction speed, due to the activating influence of the methyl group.

Coupling of aryl amines and phenols with diazonium salts is usually

aided by positive (electron-releasing) substituents in the amine or phenol ring. These groupings, when in the meta position to the amino or hydroxy group, aid distinctly in increasing the speed of the reaction.

By analogy, the 4 position in pyridine compounds can be considered equivalent to the 3 position in substituted benzene compounds (see Fig. 3).

Therefore, methyl groups, which are electron-releasing combinations, should, when substituted in the pyridine 4 position, exert an activating influence on the coupling reaction and should augment the action of the tertiary amino group present.

One exception which I cannot explain is the slightly greater depth of color found when 3 methyl pyridine (beta picoline) is reacted than when 2 methyl pyridine (alpha picoline) is combined with the diazo compound.

That the methyl group in the 2 position has an activating influence also can be explained by the fact that electronic activity is transmitted with little loss through vinyl groups. This principle of vinylology applies because the 2 and 4 positions are separated by vinyl groupings.

Since a definite orange coloration not shown by controls was given by the reaction of 2,4,6 collidine with diazosulfanilic acid, the coupling with the diazo compound must have taken place at the 3 or 5 positions—the positions meta to the pyridine nitrogen.

To test this, the same type reaction with the diazo compound was run, using, this time, dibromopyridines. Although these compounds are solids,

only slightly soluble in water, some interpretable results were obtained. With the 2,6 dibrom compound, some faint color was observed after fifteen minutes, while the 3,5 compound gave no color except that of the control tests. Although only approximate, these observations can be interpreted to mean that the azo linkage in pyridine compounds is formed in the 3 or 5 position.

Theory bears this out. In benzene compounds, amines and phenols, coupling is known to take place in the positions 2 or 4 to the amino or hydroxy substituted carbon.

Studying the coupling positions in both benzene and pyridine derivatives, one may find in certain resonant forms like linkages between the coupling position and the nitrogen connected with or in the ring (Fig. 4).

Aside from colorimetric work on these compounds an attempt was made at actual isolation.

From my experiment, it was found that the coloring material was insoluble in ether or benzene. However when acetone was added to the reaction mixture and the whole made strongly alkaline, small, deep red globules settled out of the red solution. Separated from the mother liquor, these globules were evaporated on a water bath.

The resulting mass appeared to be sodium hydroxide, intimately mixed with a red compound, probably the sodium salt of the sulfanilic acid, 2,4 lutidine azo compound. The whole was very soluble in water and not so in ether or benzene. A solution of this substance, neutralized, gave the same

color changes as the reaction mixture of the pyridine homologue and diazo-sulfanilic acid.

• • •

Within the limits of their accuracy,

I offer the results of the foregoing experiments as another bit of proof of the present theories of coupling of diazonium salts and aromatic compounds.

Sodium Aluminate

by WILLIAM LEE McLEISH, 17.

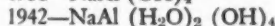
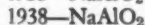
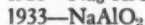
Plainville High School, Cincinnati, Ohio

► FOR MY PROJECT I chose to attempt to find the reason for a variance in the formula of sodium aluminate. My method was to measure freezing points of solutions of sodium aluminate. This would indicate the number of molecules existing in solution according to Raoult's law, which states that freezing point depressions are proportional to the number of molecules of solute. By performing the first set of experiments in water solutions, I tried to determine how many hydroxyl ions, if any, were combined with aluminum hydroxide molecules and thus did not lower the freezing point; for all my sources agreed that hydroxyl ions combined with aluminum hydroxide molecules in the reaction and some claimed that water was then given off. Therefore, a second group of experiments was planned, to be conducted in solutions other than water. Taking into account the results of the first group, I might be able to determine the amount of water given off.

I understand that it was possible to calculate the freezing point depression by simple multiplication of the molar concentration by constant. I also understand that this formula held true for electrolytes if the number of

ions was used for the concentration instead of the number of molecules, even in concentrated solutions.

Following are the formulas which I found for sodium aluminate and the date of publication of the books in which I found them:



For my first experiment I added a nearly saturated solution of sodium hydroxide to a nearly saturated solution of aluminum sulphate until the precipitate which first formed dissolved. By the means mentioned above, I calculated that the freezing point depression should be approximately 2.9° Centigrade minus 0.26° Centigrade for every hydroxyl ion that combines with an aluminum hydroxide molecule. Although I did not know it then, this is incorrect, since electrolytes and concentrated solutions do not exactly follow this formula.

Cooling my solution with a mixture of ice and salt, I measured the freezing point with a regular laboratory thermometer, which I could read to 0.25° Centigrade. A thick white

precipitate formed at -3° Centigrade, when I stirred the solution, with a rapidity and a temperature rise which suggested a supercooled solution. With continued stirring, the almost solid mixture changed to a thick slimy liquid in which the white crystals were almost invisible. The precipitate did not completely dissolve below 26° Centigrade.

When the process was repeated a precipitate did not form until I stirred the solution at 4° Centigrade. I stirred the mixture to a thinner consistency and filtered. I cooled the filtrate to -7° Centigrade without a sizeable precipitate. I analyzed this precipitate and found it to be aluminum sulphate.

In an attempt to avoid this precipitation without reducing the concentration of aluminate, I decided that I could: (a) use ions of higher valence, as calcium, thallium, ferrocyanide or citrate ions, which are less soluble and more difficult to procure; (b) use aluminum hydroxide for aluminum sulphate; or (c) use aluminum for aluminum sulphate. I decided to use aluminum because it introduced fewer ions into the solution.

Adding aluminum to a sodium hydroxide solution, I found the aluminum was not completely soluble. The residue looked like sand mixed with a black acid-soluble solid. I found nothing in a qualitative analysis which I made on the solid. Repeating the experiment with different aluminum, I dissolved 42 mg. aluminum in 5 ml. concentrated sodium-hydroxide solution. After four days there were precipitated some crystals

which were soluble after gentle heating, and the solution was slightly colored brown. After the volume was corrected, a precipitate formed at -1° Centigrade. This prevented taking a freezing point reading because it changed the concentration. Although the solution was diluted by stages to 20 ml., it still formed a precipitate below zero. This precipitate may be sodium carbonate, which is less soluble than sodium hydroxide. The sodium hydroxide may have absorbed enough carbon dioxide to cause a precipitate.

I did not repeat the experiment because at this time I made some further studies of Raoult's law and freezing points, and learned that I had been mistaken in believing that solutions of electrolytes and solutions of high concentrations had freezing points lowered directly proportional to the molar concentration. However, I also learned that solutions with the same concentrations have the same freezing point. I also found one book which stated that the presence of dissolved aluminum hydroxide does not change the freezing point of a sodium hydroxide solution. I should have saved myself a lot of trouble had I hunted this out before.

I decided to check the statement that aluminum hydroxide does not change the freezing point of a sodium hydroxide solution. I checked my thermometer for accuracy and then cooled a sodium hydroxide solution to -5° Centigrade, where I finally got a precipitate which could have been ice. Acting for the time on this assumption, I attempted to find the freezing point. Since the amount of precipitate

varied inversely with the temperature, I could not find the freezing point; but I finally found -4.1° or -4.2° Centigrade as the point where the greatest amount of precipitate dissolved. I made some aluminum hydroxide, filtered it, and dissolved a few grams in the solution. I again cooled it and met with the same difficulty, but finally found -3.2° to -3.6° Centigrade as the melting point. When the process was repeated the melting point for sodium hydroxide was -6.5° Centigrade while the melting point for the solution with aluminum hydroxide was -4° Centigrade. As I was writing my notes it occurred to me that the raised freezing point could have been due to the fact that the water added with the aluminum hydroxide had lowered the concentration of ions.

To get an idea of the difficulty of the problem of the group in which I would measure freezing points of solutions other than water, I tried to dissolve sodium hydroxide in such organic liquids as carbon tetrachloride, glycerin, and ethyl alcohol. It dissolved only in ethyl alcohol. When I added aluminum there was no reaction until I had also added water. This suggests that water is necessary for the reaction. I also added alcohol to a water solution of sodium aluminate to precipitate sodium aluminate which is said to be insoluble in alcohol.

In the future I plan to (1) use dry aluminum hydroxide in trying to determine whether it changes the freez-

ing point of a sodium hydroxide solution, (2) try to determine whether the crystals formed in the experiment with sodium hydroxide and aluminum are ice, (3) repeat the experiment using aluminum and sodium hydroxide, and whatever experiments these experiments suggest.

Experiments made for this project to date have been:

- 1—An attempt to measure the freezing point of a solution formed by adding sodium hydroxide to aluminum sulphate. I analyzed this precipitate and tried to measure it.
- 2—An attempt to measure the freezing point of a solution made by adding aluminum to a sodium hydroxide solution. I found an unidentified impurity in the aluminum.
- 3—A repetition of No. 2 using purer aluminum (It was allowed to set too long).
- 4—An attempt to measure the freezing point of a solution made by adding aluminum hydroxide to a sodium hydroxide solution, but aluminum hydroxide precluded correct measurements by being wet.
- 5—Several preliminary experiments in organic solutions.

None of these attempts have closed the way to further work in this field. I shall continue along the lines indicated above. After this project I plan to work on such other projects as making a viscosimeter, making a radiometer and making other devices.

► *YOUNG SCIENTISTS who come as trip winners to the Science Talent Institute in Washington bring samples of the projects they are working on, and set them up for Hobby Night. Shots of some of these exhibits enliven the back cover of this month's CHEMISTRY.*

Collection of Rare Elements

by WILLIAM ROBERT RENNAGEL, 16
Eden Central High School, Eden, N. Y.

► THE IMPORTANCE of the common chemical elements to modern civilization is obvious. Not only are the common elements necessary for life, but they are also necessary for civilization. Chlorine is used as an antiseptic and a bleach; in the form of sulfuric acid, sulfur is the cornerstone of the chemical industry; without nitrogen, we could not produce any explosives; phosphorus is a necessary ingredient in matches; the hydroxides of the alkali metals are needed to make cleaning agents; and were it not for the heavy metals, we should still be in the Stone Age. These are but a few of the innumerable uses to which the common elements are put.

Despite the fact that they are not necessary for life, many of the elements which we consider as rare are also very important to modern civilization. Cesium and rubidium are used in the manufacture of various kinds of electronic tubes; beryllium raises the fatigue endurance of alloys; indium is used in jewelry; thallium compounds can be found in many poisons for insects and rodents; an alloy of cerium is used in flints for cigarette-lighters; and titanium and vanadium are important components in many modern steel alloys. Each of these elements also has many uses other than those mentioned here.

The rare elements are not so rare as they are generally thought to be. I have compounds of almost sixty chemical elements and yet none of these

was really difficult to obtain. There are several chemical companies which specialize in the compounds of the rare elements and I obtained many of mine from one such company. The rest of my compounds of rare elements were obtained from large chemical companies which stock a few rare compounds. Although the most expensive compounds cost more than a dollar a gram, the majority of rare compounds cost about seventy-five cents an ounce. Since I was able to purchase not only rare compounds but also other chemicals, apparatus, and books with a salary of two dollars a week, it is evident that to study the rare elements is not a very expensive hobby.

My present research in the chemistry of the rare elements is not intended to be exhaustive. At most it is just a beginning from which I can make a more thorough study of the rare elements at a later time. All of my work so far has been concerned merely with test-tube reactions, and then only with the commoner compounds of the rare elements mentioned in this discussion. In the case of the rare metals which give positive ions in solution, I tried to precipitate the hydroxide, the carbonate, the phosphate, and the chromate of each metal. In the case of the rare elements which give negative ions in solution, I tried to precipitate the barium, calcium, copper, ferrous iron, ferric iron, and lead salts of each acid radical. Occasionally I tried to precip-

itate other compounds. When any salt of a rare element is not mentioned, it is because either that salt is soluble in water, or it is merely a white precipitate, or I did not try to precipitate it.

The Alkali Metals

Lithium.—Both the carbonate, Li_2CO_3 , and the phosphate, Li_3PO_4 , are white precipitates. I tried three times to precipitate lithium carbonate, but I did not succeed until the third time. Both these salts are slightly soluble in water and do not precipitate unless concentrated solutions are used in preparing them. Evidently not enough lithium chloride or sodium carbonate was used the first two times I tried to prepare lithium carbonate.

Cesium and rubidium.—The only salts of these elements which can easily be precipitated are the bitartrates and the chlorplatinate. Having no sodium bitartrate, I could prepare only the chlorplatinate. The reaction which occurred when I prepared cesium chlorplatinate is easy to understand, since it is merely an addition reaction: $2\text{CsCl} + \text{PtCl}_4 \rightarrow \text{Cs}_2\text{PtCl}_6 \downarrow$, but the one which occurred when I prepared rubidium chlorplatinate is probably very complicated, since my rubidium compound is the carbonate and yet no obvious action other than the precipitation of the rubidium chlorplatinate occurred. Perhaps this is the reaction that took place: $6\text{Rb}_2\text{CO}_3 + 3\text{PtCl}_4 + 3\text{H}_2\text{O} \rightarrow 2\text{Rb}_2\text{PtCl}_6 + \text{Rb}_2\text{PtO}_3 + 6\text{RbHCO}_3$. Both cesium and rubidium chlorplatinate are light yellow precipitates.

Beryllium.—Beryllium hydroxide, $\text{Be}(\text{OH})_3$, is a flocculent white precipitate soluble in beryllium sulfate, BeSO_4 . It dissolves in an excess of

sodium hydroxide, forming sodium beryllate, Na_2BeO_2 . Beryllium carbonate, BeCO_3 , and beryllium phosphate, $\text{Be}_3(\text{PO}_4)_2$, are flocculent white precipitates. Beryllium chromate, BeCrO_4 , is soluble, but its solution is darker in color than that of potassium chromate.

The Earths

Indium.—Indium carbonate, $\text{In}_2(\text{CO}_3)_3$, is a white precipitate. When I prepared it with indium chloride and sodium carbonate, a gas was released. Probably it was carbon dioxide, but I had no way of testing such a small quantity of the gas. Indium chromate, $\text{In}_2(\text{CrO}_4)_3$, is a yellow precipitate. The phosphate, InPO_4 , is a bluish-white precipitate. The hydroxide, $\text{In}(\text{OH})_3$, is a heavy, flocculent white precipitate.

Thallium.—Thallium sulfide, Tl_2S , is a black precipitate. The chromate, Tl_2CrO_4 , is a yellow precipitate. The carbonate, Tl_2CO_3 , and the phosphate, Tl_3PO_4 , are both soluble. Thallium chloride, TlCl , is a heavy white precipitate. Thallium bromide, TlBr , is a creamy white precipitate. Thallium iodide, TlI , is a heavy yellow precipitate. Potassium permanganate gives a reddish brown precipitate with thallium sulfate, Tl_2SO_4 .

Yttrium.—The carbonate, $\text{Yt}_2(\text{CO}_3)_3$, and the phosphate, YtPO_4 , are white, flocculent precipitates. The chromate, $\text{Yt}_2(\text{CrO}_4)_3$, is a yellow precipitate. Yttrium hydroxide, $\text{Yt}(\text{OH})_3$, is a white gelatinous precipitate.

Lanthanum.—The carbonate, $\text{La}_2(\text{CO}_3)_3$, and the phosphate, LaPO_4 , are white precipitates. Lanthanum hydroxide, $\text{La}(\text{OH})_3$, is a white, floccu-

lent precipitate. Lanthanum chromate, $\text{La}_2(\text{CrO}_4)_3$, is a yellow precipitate.

Cerium.—Cerous carbonate, $\text{Ce}_2(\text{CO}_3)_3$, and cerous phosphate, CePO_4 , are white precipitates. Cerium hydroxide, $\text{Ce}(\text{OH})_3$, is a flocculent white precipitate. Potassium chromate produces a yellowish-brown precipitate with cerium nitrate. The precipitate probably contains ceric compounds and reduction products from the chromate. The addition of hydrogen peroxide to a solution of cerous nitrate changes it to basic ceric nitrate: $2\text{Ce}(\text{NO}_3)_3 + \text{H}_2\text{O}_2 \rightarrow 2\text{CeOH}(\text{NO}_3)_3$. Sodium hydroxide with basic ceric nitrate produces a reddish precipitate probably containing some ceric hydroxide, $\text{Ce}(\text{OH})_4$, and a gas, probably oxygen.

Titanium.—The trioxide, Ti_2O_3 , is a grayish-blue precipitate. Potassium chromate produces a bright yellow precipitate with titanium trichloride, TiCl_3 . Sodium carbonate produces a bluish-purple precipitate and a gas, probably carbon dioxide, with titanium trichloride. Titanium phosphate, TiPO_4 , is a purple precipitate. Hydrogen peroxide produces a reddish-orange precipitate, probably titanium peroxide, TiO_3 , with titanium trichloride. Sodium sulfite gives a light yellow precipitate. Stannous chloride gives a blue-gray precipitate.

Zirconium.—The carbonate, ZrOCO_3 , is a white precipitate. The phosphate, $(\text{ZrO})_3(\text{PO}_4)_2$, is a white precipitate. The chromate, ZrOCrO_4 , is a yellow precipitate. Zirconyl hydroxide, $\text{ZrO}(\text{OH})_2$, is a white, flocculent precipitate.

Thorium.—The carbonate, $\text{Th}(\text{CO}_3)_4$, and the phosphate, Th_3

$(\text{PO}_4)_4$, are white precipitates. The chromate, $\text{Th}(\text{CrO}_4)_2$, is a yellow precipitate. Thorium hydroxide, $\text{Th}(\text{OH})_4$, is a flocculent white precipitate.

The Amphoteric Elements

Vanadium.—Ammonium vanadate, NH_4VO_3 , the vanadium salt which I possess, is only slightly soluble in water but is quite soluble in sodium hydroxide solution. The acid and the salts mentioned were prepared by the use of such an alkaline solution. Vanadic acid, HVO_3 , forms a yellow solution when an acid is added to an alkaline solution of ammonium vanadate. Calcium vanadate, $\text{Ca}(\text{VO}_3)_2$, is soluble. Copper vanadate, $\text{Cu}(\text{CO}_3)_2$, is a light green precipitate. Ferrous vanadate, $\text{Fe}(\text{VO}_3)_2$, is a bluish-black precipitate. Ferric vanadate, $\text{Fe}(\text{VO}_3)_3$, is a reddish-brown precipitate. Lead vanadate, $\text{Pb}(\text{VO}_3)_2$, is a heavy yellow precipitate.

Uranium.—Potassium uranate, $\text{K}_2\text{U}_2\text{O}_7$, is a bright yellow precipitate. Uranyl phosphate, UO_2HPO_4 , is a yellowish-white precipitate. Uranyl sulfate, UO_2SO_4 , is soluble. There was no visible reaction between uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2$, and sodium carbonate or potassium chromate.

Selenium.—Barium selenate and calcium selenate, BaSeO_4 and CaSeO_4 respectively, are white precipitates. Ferrous selenate, FeSeO_4 , is a greenish-white precipitate. Ferric selenate, $\text{Fe}_2(\text{SeO}_4)_3$, is a light yellow precipitate. Cupric selenate, CuSeO_4 , is a light green precipitate. Lead selenate, PbSeO_4 , is a heavy white precipitate.

Tellurium.—Telluric acid, the tellurium compound which I used, is only very slightly soluble in water.

Hence none of the reactions in the preparation of the salts mentioned here was very satisfactory. Barium tellurate, BaTeO_4 , is a white precipitate. Copper tellurate, CuTeO_4 , is a light blue precipitate. Lead tellurate, PbTeO_4 , is a white precipitate. I was able to precipitate either ferrous or ferric tellurate.

How soon I can do more research in the chemistry of the rare elements I do not know. I do not expect to have much time for chemical research during the next few months. When it is

possible for me to do so, I should like to begin work on another project, one that will be much more complete than its predecessor. I intend to take each element separately and try to prepare all the compounds I can of that element. In this way I may make an important discovery. Whether or not my work proves to be useful to other chemists, I still have the satisfaction derived from doing it. Fame is worthless without satisfaction, but satisfaction is valuable in itself.

The Extraction of Natural Products

by JAMES WILLIAM WILT, 16.
De La Salle High School, Chicago, Ill.

► THROUGH SIX YEARS of chemistry, though surrounded by all the wondrous works of man, I have concluded that chemistry at its greatest is to be found in the works of nature. For nature embodies every type of chemical procedure. It synthesizes products impossible to man. To arrive at the precision and versatility with which nature performs has always been the ultimate goal of science. Whether or not science achieves this goal time alone shall tell, for compared with the magnitude of nature's laboratory and the number of compounds produced, science is yet in its infancy.

Convinced of the "land of plenty" which awaited me in the products of nature, I set out to utilize what was contained in them for the advancement of my knowledge of nature.

Early this summer, while studying the different variations of the Diels-

Alder synthesis, I saw a chance to use what nature offered in preparing maleic anhydride, the necessary reagent in the synthesis. Since this synthesis produces many interesting compounds by coupling the maleic anhydride with conjugated double bonds, an extraction which would obtain the maleic anhydride might prove profitable.

Unripe berries contain an appreciable amount of malic acid, the parent compound of maleic acid. Therefore, I decided to gain knowledge and experience by extracting malic acid from unripe berries.

Since it is especially fine in its content, I chose the mountain ash tree as the source of the berries. During late June and early July I picked all the berries from a nearby ash tree. Of a green color, their juice gave a distinct acid reaction on litmus paper. I crushed the berries to a fine pulp

in a meat grinder, collecting all the juice expressed. Boiling both the pulp and the procured juice with water, I obtained, on filtering, a clear liquid with a slight greenish tint. Again litmus and congo-red papers proved its acidity.

The removal of the acid from its solution should consist in precipitating its insoluble calcium salt and decomposing this salt with a suitable acid. Accordingly, I boiled the solution, adding slowly and in a fine stream, calcium hydroxide until the liquid was neutral. The mixture turned brown and calcium malate was precipitated. The supernatant liquid was withdrawn and the malate left to dry.

Afterwards, the malate so prepared was stirred into a hot, dilute solution of nitric acid, which served to partially reduce the malate, forming calcium hydrogen malate. This fell to the bottom from the reactants as light brownish crystals.

A solution containing a calculated amount of the hydrogen malate was then decomposed by slowly adding, with stirring, the theoretical quantity of oxalic acid in solution. The insoluble calcium matter was removed by filtration and the remaining liquid evaporated to crystallization.

The acid obtained was slightly tinted and required one or two re-

crystallizations, accomplished easily from hot water. So purified, it was clear and formed fairly large crystals.

Perhaps the only disadvantage in the entire process was the great number of berries required for a workable yield. I began with one hundred grams of berries and received a yield of three grams of malic acid. Considering the acid content of the berries as four percent, the yield was seventy-five percent of the theoretical.

Thus, in malic acid I had the immediate source of the maleic anhydride required for the Diels-Alder Synthesis. As a result, I could convert the malic acid to maleic anhydride at any time through the usual method, using heat and acetyl chloride. (The main reactions are shown in Fig. 1.)

This first preparation has suggested many more, as, for instance, the isolation of citric acid from lemons, and the isolation of tartaric acid from grapes. I hope to complete these various fruit-acid isolations in the near future, for I believe any naturally occurring acid may be had by the above method or a modification of it.

Some months later I had occasion to call upon nature once again. During an investigation of the Knoevenagel synthesis, I came in need of some

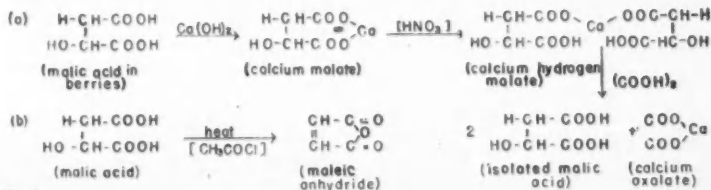


Fig. 1.

piperidine, a hydrogenated pyridine compound. Used as a catalyst, it activates the various groups involved in the molecular condensations which make up the reaction.

As I recalled my extraction of malic acid in early summer, I resolved then to obtain piperidine for the synthesis from a natural product also. Finding in reference books that black pepper contained an alkaloid related to piperidine, called piperine, in small amounts, I was ready to start. If I could split the piperine into its component fractions—piperidine and piperic acid—and withdraw the acid, I would have the needed piperidine.

This one step, however, was not easy. It was a long and arduous task before I finally succeeded in capturing a small amount of piperidine. I shall attempt to simplify this extraction soon.

Starting with twenty grams of ground black pepper, I extracted the

alkaloid piperine under reflux with hot alcohol. The greenish solution was filtered and evaporated down to a few milliliters.

Adding one gram of potassium hydroxide to every five milliliters of liquid, I cautiously distilled the frothing mixture, collecting all of the clear distillate.

I then neutralized this distillate with dilute hydrochloric acid and evaporated it quickly to dryness under a vacuum. Since the powder which remained was contaminated with ammonium chloride formed by various reductive side-reactions, it was refluxed once again with hot alcohol to remove the piperidine hydrochloride from the ammonium chloride. On the removal of the alcohol, again under a vacuum, there remained one-half gram of piperidine hydrochloride.

This is an over-all yield of sixty-three percent of the theoretical. (The main reactions are shown in Fig. 2.)

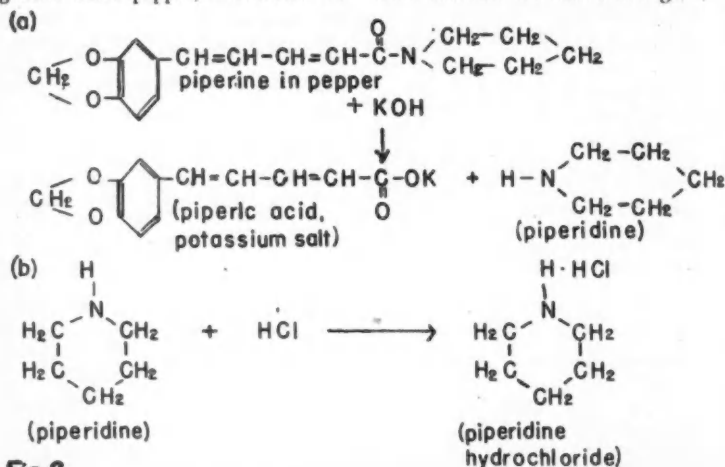


Fig. 2.

As the Knoevenagel synthesis requires only a minute amount of piperidine, I look upon this extraction of it from pepper as one of my most satisfying preparations.

Thus, this year I have performed two extractions from natural products, both with gratifying results. I shall extend these extractions greatly, for they constitute a major portion of my aims in the field of organic chemistry. It is a field which shall know no limits. But even now, here in the present, great strides are being made

in the direction of understanding the hows and whys of nature. I firmly believe that when man better knows how natural chemical phenomena occur, he can move forward to duplicate these reactions with much more confidence in himself and in his success.

It is my fond hope that I may be among the ranks of these men, doing my part to make clear the complex picture of nature which confronts us now.

Refined Food Backed by Tests

► REFINED foods, such as white bread, may not be so inferior to more crude foodstuffs as nutrition and health authorities have long believed and taught. The first experimental contradiction to this idea is reported by Drs. George H. Hitchings and Elvira A. Falco, of the Wellcome Research Laboratories.

Mice on a diet of white bread were more resistant to pneumonia than mice on a whole wheat bread diet, they found. Only one of 49 mice on the whole wheat diet survived the disease, whereas 20 of the 50 eating white bread survived. Both groups of mice were given the same size dose of pneumonia germs for the tests.

The experiments, the scientists point out, do not give enough evidence to decide the white vs. whole wheat bread controversy. Neither are they sufficient for basing a dietary treatment of pneumonia. They do

"cast considerable" doubt on the belief that when known diet essentials are present in equal amounts, the crude foodstuff is preferable to the refined. The idea back of this belief is that the crude foodstuffs may contain unknown factors which are "always beneficial."

The results reported by the scientists are interesting in view of other studies in recent years showing that the better fed animals are, the more susceptible they are to certain germ infections. Scientists have almost been ready to go back to the old adage, feed a cold and starve a fever, with the idea of depriving a patient during acute germ disease of food factors, such as vitamins, which the germs as well as the patient needs. The hope would be to starve the germs out before the patient suffered too severe vitamin starvation. Whether refined foods are the means for doing this remains for future studies to decide.

Chemical Things To Do

Compass From Dead Flashlight Cell

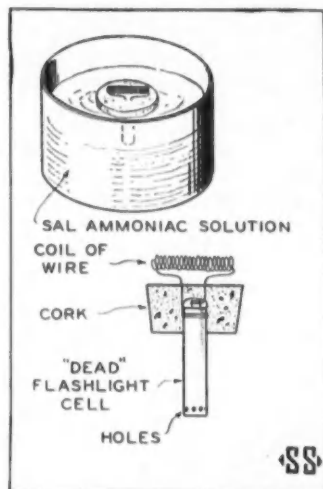
by JOSEPH H. KRAUS

► AN ELECTRO-MAGNETIC compass can be made with a "dead" flashlight cell, wire and cork. This is because a coil of wire through which current flows tends to align itself in a true north-south position. An old flashlight cell can be made to furnish enough current for the experiment. The cell and coil are supported in water by a cork or wooden block.

A flashlight cell which is too weak for use should be selected for the experiment. Cut a hole in the bottom of a cork or wooden float as illustrated in the diagram. It should be just large enough to fit the cell. If the hole should become slightly larger, the cell can be held securely in place by snapping a few rubber bands around the outer zinc case.

Punch in the cork two small holes through which you can thread the ends of a six-foot length of copper wire to connect with the battery. Bell wire from an old electric bell or heavier announcer wire may be used. Bare one end of the copper wire, push it through the hole and wrap around the carbon or center electrode of the cell. With some flashlight cells it may be necessary to break away a little of the compound to obtain a better gripping surface.

About one inch or so above the cork, start wrapping the wire in a spiral around a pencil. Bare the free end, exposing the copper surface of



the covered wire, and wrap it several times around the case of the flashlight. Now push the flashlight cell into the cork and seal with wax so water will not get near the terminal. Float the whole unit in the center of a large vessel of water. Although a drinking glass may be used, the float tends to come to rest against the sides of the glass, thus interfering with its free movement.

Float Turns in Water

If a little current flows through the coil of wire, the float will gradually turn until one end points to the north magnetic pole, the other to the south. Make some distinguishing mark on the end of the coil that points north.

This end will always point north, no matter where you try the experiment.

If your cell is completely "dead," however, and no current flows through the coil, it will assume a static position instead of turning to point to the north-south position. You can, however, refresh the cell so it can be used.

If no current flows, punch a few holes through the bottom of the flashlight cell. This can be done with an ice-pick. Stir about an ounce of sal ammoniac into a glassful of water, set your flashlight cell into the solution for about a half-hour, then remove the

cell and place in the larger container of water, or just stir in four ounces of sal ammoniac to each quart of water in your large container and set your float in this solution. Frequently cells treated in this way will furnish enough current to make the wire coil align itself with the magnetic lines of force of the earth.

If you want a more effective compass that will come to rest a little more quickly, use larger wire and put more turns in the coil, making the coil longer. Be sure, however, that the coil is horizontal and does not sag in the middle.

New Water Disinfectant

★ WATER from GI canteens in the future will be safer and taste better, thanks to a new disinfectant tablet which uses iodine instead of chlorine to purify the water.

Chlorine and chlorine compounds, stand-bys in water disinfection for almost 40 years, as ordinarily used cannot be counted on to protect troops in the field from amebic dysentery or schistomiasis. The parasites of these diseases when in the cyst stage are too resistant to disinfection by such means. It would take at least six standard Halazone tablets, for example, to disinfect a canteen of warm water in 36 minutes. After this treatment, the soldier probably would not drink the water because of the unpleasant taste. Even with strict supervision, it was sometimes difficult to keep soldiers from drinking water from streams or wells of doubtful purity, rather than use the chlorine-disinfected water.

Search for more satisfactory canteen

disinfectants was led during the war by Dr. Gordon M. Fair of Harvard under OSRD contracts. Quarternary ammonium compounds and triiodides were investigated. One of the latter, triglycine hydroperiodide, was finally selected by the Quartermaster Corps as having the highest military characteristics.

Tablets of this dissolve quickly, liberate seven and one-half parts per million of elemental iodine, enough to kill quickly the cysts of amebic dysentery germs and to reduce the number of typhoid, cholera and bacillary dysentery germs from about 100,000,000 to five or less per 100 cubic centimeters of water.

Soldiers and marines who tried the tablets did not object to the taste or odor of the water. Additional tests of the new "tablet, water purification, individual, iodine," will be carried out during the coming year.

New Patents by Chemists

With the first issue of the new year, the Official Gazette of the U. S. Patent Office appeared in a new dress. The rather prosaic typography that characterized its cover in the past has been changed for a more imaginative design that makes it look like one of the quality-group magazines or a learned quarterly.

Copies of patents may be obtained from the U. S. Commissioner of Patents, Washington 25, D. C. Order by number and enclose 25 cents (not in stamps) for each patent desired.

► AN INVENTION of interest to those concerned with deep wells is a method of determining the permeability of the earth formation penetrated by a well bore. This is done by determining the rate at which a given fluid can be made to enter any particular section of the bore. Patent 2,413,435 was granted Leo A. Courter of Seminole, Okla., for the method; it is assigned to the Dow Chemical Company, Midland, Mich.

To Clean Aluminum

► CLEANING COMPOSITION for aluminum and aluminum alloys for removing oxide films contains ammonium silico-fluoride and sodium acid sulfate. It has enough ammonium sulfate to prevent the formation of a precipitate in water solutions of the cleaner. The patent, 2,413,365, was awarded to Lowell R. McCoy, Detroit, and is assigned to Wyandotte Chemicals Corp., Wyandotte, Mich.

Pavement Reconditioner

► WITH THOUSANDS of miles of worn and neglected highway and street pavements to be replaced, more than usual interest attaches to a steam reconditioner for bituminous cinder material, making possible the re-use of old surfacings. This machine, the invention of W. F. Chester of Bayside, N. Y., is protected by patent 2,413,908.

It is of quite simple construction, consisting of a sealed hopper containing a superposed series of perforated steam pipes in grid-like patterns. The broken-up pavement material is thrown into this, and the steam, at fairly high pressure and temperature, digests the bituminous binder out of the mass. At the same time, new pavement materials are added. Preliminary analyses are necessary to determine the needs for each stretch of road.

Self-Contained Spray-Gun

► A SPRAY-GUN for insecticides, fumigants, etc., which contains its own motor-driven compressor is the subject of patent 2,413,710, granted to John P. Jason of Chicago. The power cord leads in through the pistol-grip handle. A float in the reservoir automatically cuts off the motor when the supply of liquid is exhausted.

Glass Tempering

► A METHOD for tempering glass sheets by rapid cooling was developed by a Frenchman, Bernard Long, of Paris, and covered by patent 2,413,722.

The glass, while still hot, is passed between slotted tubes from which issue even, sheet-like streams of cooling air. This eliminates the unequal cooling that often produces iridescent spots on the glass.

For Light Metals

► **HEAT TREATMENT** for light metals, on which patents 2,413,928 and 2,413,929 have been issued to James F. Simpson of the American Cyanamid Company, has as an essential step immersion in a bath consisting mainly of potassium cyanate.

Fish Processing

► **FLOATING** fish factory, patented by L. B. Harris of Southold, N. Y., is a ship, with processing equipment forward, propulsion machinery amidships and refrigerating space aft. This permits fish to be dressed at sea, as soon as caught. The patent number is 2,413,918.

Improving Leather

► **WEAR-RESISTING** leather is made more durable by impregnation with a water-insoluble synthetic resin. Patent 2,413,806 has been issued on this to George Virtue of Boston.

Glass Wings for Cinderella

► **AIR-AGE** Cinderellas will go to the ball not in glass slippers but on glass wings, if the plane-construction design offered for patent 2,414,125 by George B. Rheinfrank, Jr., of Perrysburg, Ohio, comes into widespread use. Intended primarily for light planes, it builds up wings and other load-carrying parts by plastic-bonding multiple layers of glass fabrics over cores of balsa wood. Nylon or rayon may be used instead of glass fiber, the inventor states.

New Insecticide

► **AN OIL-SOLUBLE** compound of copper and nicotine, suitable for dissolving in hydrocarbons to enhance their insecticidal properties, is the chemical invention of Claude R. Smith of the Eastern Regional Research Laboratory, U. S. Department of Agriculture. Rights in his patent, No. 2,414,213, have been assigned, royalty-free, to the government.

Saving Selenium

► **REDUCING WASTE** of the rather costly element selenium when it is added to molten glass for the purpose of obtaining a tinted product, is the objective of patent 2,414,413, issued to A. E. Pavlish and C. R. Austin of Columbus, Ohio, assignors to the Battelle Memorial Institute. Adding an oxidizable silicon compound along with the selenium prevents most of the loss through volatilization that occurs when selenium is put in alone.

Better Beer Quicker

► **BEER** of better flavor, more quickly made, is promised by a new continuous-process method on which U. S. Patent 2,414,669 has been issued to Gustave T. Reich of Philadelphia.

Instead of adding broken or ground malt to cooked rice or other starch early in the process, as is traditionally customary, this brewmaster leaves the malt unbroken until its maximum diastase content has been developed, then adds it quickly to the cooked starch mass that is to be saccharified. By refraining from breaking the hulls on the malted grain until the last possible moment, Mr. Reich explains, he minimizes the release of unpalatable flavors into the wort.

After the finely ground malt and

the finely ground starch mass have been mingled, and the latter turned into fermentable sugars, the brewing process follows conventional lines.

Food Dehydration

► CONTINUOUS-PROCESS dehydration of foods is covered by patent 2,414,580, taken out by Clarence Birdseye of Gloucester, Mass., pioneer in several modern food-handling methods. Chopped meat or fish, or finely cut vegetables, are spread on an endless conveyor belt of thin stainless-steel sheet. They are subjected first to radiant heat from infra-red lamps, or to intense high-frequency radio waves. This initiates the dehydration process, which is then completed by a current of heated air or other gas. At the end of the run, the finished product is scraped off the metal belt by a fixed knife.

Waste From Coal

► WASTE PRODUCTS from furnaces burning powdered coal can be put to economic use as light-weight aggregate in concrete mixing, by a method on which patent 2,414,734 has been granted to Louis Gelbman of Yonkers, N. Y.

Instead of pit-ashes and clinkers, powdered-coal furnaces produce a glassy waste that is practically ready for use "as is." The fine fly-ash, prevented from escape up the chimney only by electric precipitation, presents more of a problem because of its combustible residues which are difficult to burn out by ordinary methods. In Mr. Gelbman's setup, fly-ash is sintered by mixing with a certain quantity of already-sintered waste, which permits access of air to complete combustion. The sinter mass is then ground, ready for the concrete mixer.

Tar Weed Killer

► A WEED-KILLING method that looks drastic but probably effective is covered by patent 2,414,640, assigned to the Standard Oil Development Company by H. G. M. Fischer of Westfield, N. J. It consists of a mixture of reduced cracking coal tar and light oil distillate. Poured on the ground at the rate of about one-half gallon per square yard, it forms a hard crust, killing any vegetation that may be present and preventing new plants from getting started.

Leak Detector Uses Helium

► A LEAK detector to test high vacuum systems operates by showing the presence of helium, this gas being used as a tracer. It is sensitive enough to measure the normal content of helium in the air, which is approximately one part in 200,000. It also would detect a leak passing only one cubic centimeter of helium every 16 years, it is claimed.

The leak detector is a product of the General Electric Company. In testing

vacuum systems, the new device used either a jet or envelope method. In the former, a small jet of helium is moved over a suspected leak area. If the jet passes over a leak, an indicating needle deflects on the detector. The leak is located within $\frac{3}{8}$ inch.

In the envelope method, the vacuum system being tested with helium is enclosed. The instrument indicates the presence of a leak, but does not point out the exact location.

For the Home Lab

Aspirin

by BURTON L. HAWK

► UNDOUBTEDLY the most popular and most widely used drug of its kind, aspirin has been used to relieve discomfort and pain since 1900 . . . so we read on the label of the aspirin bottle. Chemically known as acetylsalicylic acid, it acts as an *analgesic* which removes pain, and as an *antipyretic* which reduces the body temperature. Thus it finds use in the treatment of rheumatism, arthritis, influenza, neuralgia, tonsillitis, neuritis, fevers, lumbago, and, of course, headache.

You can prepare aspirin without too much difficulty in the home lab for demonstration purposes. However, for practical purposes we recommend purchasing the aspirin from the drug store.

Carefully mix together 2 cc. of acetic anhydride and 2 cc. of acetic acid. Pour the mixture into a small flask and add 2 grams of salicylic acid. Boil the solution gently for about ten minutes. What we are doing here is simply adding a dash of "acetyl" to the salicylic acid thus producing acetylsalicylic acid. Pour the hot solution into a beaker of cool water, whereupon the aspirin will crystallize out of solution.

If you add a few drops of ferric chloride solution to a solution of salicylic acid you will notice a deep violet coloration. Pure aspirin does not give this coloration thereby providing a convenient test to determine

the purity of your product. Filter off the solution, carefully dry the crystals, and recrystallize from hot water. Repeat this operation several times, then test with ferric chloride solution. It is rather difficult to remove all traces of salicylic acid from the aspirin produced by this method. If you insist on a purer product, however, dry the crystals again thoroughly and dissolve in benzene. Filter and allow the filtrate to evaporate. (Do not heat). After the liquid has evaporated, dissolve a few of the crystals in warm water and add a drop of ferric chloride solution. By this time your patience is probably exhausted, so let us proceed to another phase of our investigation of aspirin.

Salicylic Acid from Aspirin

We can also work in reverse and, using aspirin as the starting point, prepare salicylic acid. Grind an aspirin tablet to a fine powder and dissolve a portion of it in warm water. If the aspirin is entirely free of salicylic acid, ferric chloride should give no coloration. Add 10 cc. of sodium hydroxide solution to an equal quantity of the aspirin solution and boil the mixture for 5 or 10 minutes. The alkali converts the acetylsalicylic acid into sodium salicylate and sodium acetate: $\text{CH}_3\text{-COOC}_6\text{H}_4\text{COOH} + 2\text{NaOH} \rightarrow \text{CH}_3\text{-COONa} + \text{HOC}_6\text{H}_4\text{COONa} + \text{H}_2\text{O}$. Allow the solution to cool, then add dilute sulfuric acid. Salicylic acid will be precipitated. Filter off the solution, recrystallize from hot water and again

add a few drops of ferric chloride solution. Tattle-tale violet will identify the product!

The sodium salt of salicylic acid is also used in medicine. However, it is absorbed so readily in the stomach with resultant nausea, that other derivatives without this disadvantage are preferred. The phenyl ester of salicylic acid is such a derivative, known commonly as *salol*. Salol is used in the treatment of diarrhea, dysentery, typhoid fever, etc.

Oil of Wintergreen from Aspirin

Another salicylic derivative used in medicine is methyl salicylate, alias synthetic oil of wintergreen, betula oil, sweet birch, or teaberry oil. It is widely used in ointments and rubbing compounds for treatment of rheuma-

tism, arthritis, lumbago, and similar disorders.

Grind another aspirin tablet to a powder and place in a dry test tube. Add 2 cc. of methyl alcohol and then, cautiously, 2 cc. of con. sulfuric acid. Warm the tube gently for a few minutes. You will soon recognize the odor of wintergreen.

The above reaction provides a good test for aspirin and salicylates. Many drugs are composed chiefly of aspirin and sold under numerous trade names. If you have any tablets that you suspect may be aspirin you can perform the test as described above. Whenever testing strange compounds, you must remember to use *very small* quantities and, of course, keep your face away from the mouth of the tube.

Choose Plant Poison Carefully

► PLANNING CHEMICAL WARFARE against weeds requires a good deal of botanical know-how, Prof. A. S. Crafts of the University of California College of Agriculture points out. Each plant family has its vulnerable spots and also its special resistances to poisoning, and the chemical campaigner simply has to know what these are in any given combination of weeds to be killed and desirable plants to be spared.

Easiest and now most familiar case is killing dandelions in a lawn with 2,4-D. Dandelions have broad, flat, easily wetted leaves, and exposed, highly sensitive growing points. Grasses have narrow, upright leaves with water-resistant coatings, and their growing points are covered by the

leaf-bases. So although 2,4-D actually is harmful to grass, the weak spray that can kill dandelions is shed by grass without particular damage.

Suppose a near-reversal of the lawn case: a truck-grower's field of lettuce or endive, which are near relatives of the dandelion, with wild grasses invading as weeds. Obviously, 2,4-D won't serve here; it would kill the paying crop. But lettuce is chemically resistant to certain oils that kill grasses when sprayed on them. So a different weapon is indicated.

There are scores of potential chemical weapons in the plant scientist's armory, says Prof. Crafts. But each one must be given its proving-ground test before being released for general use.

New Physiological Effects Brought About by Synthetics

Chemicals Change Body Reactions

► EVOLUTIONARY CHANGES in mice, produced by a chemical compound, methylcholanthrene, were announced before the recent meeting of the American Association for the Advancement of Science by Dr. L. C. Strong of Yale University School of Medicine.

Chemistry thus joins physics, as represented by X-rays, radium radiations, ultraviolet rays and heat, all of which have been successfully used during the past quarter-century in speeding the production of those sudden evolutionary jumps known as mutations. For pioneer work of this kind with X-rays, Dr. H. J. Muller of Indiana University recently received a Nobel prize.

In his experiments, Dr. Strong used three strains of uniformly brown-coated mice, which by the end of the research had been inbred for twenty-five generations. The chances of their being of non-uniform heredity were thus minimized.

After satisfying himself of the genetic dependability of the mouse strains, he began injecting doses of the chemical, and watching for signs of hereditary change, particularly in the direction of cancer production. He selected among the progeny for mice that showed cancer resistance. Several breeding lines showed improvement in this respect for a number of generations but then began to backslide, reverting to the original degree of cancer susceptibility in a few more

generations. One line, however, kept the gain in resistance it had made, and still has it.

Other mutations thus chemically produced included change from the uniform brown color all over the body to a different color on the underside. These changes range from what Dr. Strong termed "pale black" to cream-color. Some of the lines developed spotted coats, and at least one strain now has white ears.

Most striking of the results would appear to be the rate of mutation, which was greatly speeded by the chemical. Use of a group of chemical warfare agents, the nitrogen mustards, for producing mutations has recently been reported. However, Dr. Strong stated, the effects of these chemicals more nearly resemble those of physical agents like X-rays.

Pests Poisoned Indirectly

► BEDBUGS, mosquitoes, ticks and other blood-sucking pests may in future be controlled by feeding an insecticide, such as gammexane, to animals. The insects would then get their poison dose from the blood they sucked when feeding on an animal.

Success in preliminary trials of this super-Borgia scheme for controlling insects is reported by Dr. Botha De Meillon, entomologist of the South African Institute for Medical Research.

He mixed powdered gammexane, which is a super-DDT, with agar and

let this jelly-like material set. It was cut in cubes and one cube fed to a rabbit every morning. Bedbugs in all stages fed fully on the rabbit and showed signs of paralysis immediately after. Not all died, but in his report to the scientific journal, *Nature*, Dr. De Meillon states:

"A colony of bedbugs would have little chance of surviving many generations if they feed continuously on a gammexane rabbit."

Yellow-fever mosquitoes fed fully and became paralyzed. All fully fed females died within 24 hours.

Ticks apparently notice that something is wrong because they do not feed fully on the rabbit with gammexane in its blood. They detach themselves and show obvious signs of distress. Most obvious of these signs are incoordination and inability to walk in a straight line away from light. The signs persist for days and within 10 days all the ticks in the experiment were dead.

Whether animals would be poisoned by feeding continuously on gammexane has not yet been determined. If they are not, or if some other chemical

that kills insects but is safe for animals is developed, the method should prove valuable for controlling blood-sucking insects. Dr. De Meillon points out that it would have great possibilities in the veterinary sphere.

Chemical Reinforces Drug

► **BETTER TREATMENT** for rheumatic fever may result from an innovation suggested by Dr. Hugh R. Butt of the Mayo Clinic. This consists in giving para-aminobenzoic acid, a member of the vitamin B complex familiarly known as PABA, with salicylates, drugs used for rheumatic fever treatment for three-fourths of a century.

Good results with this combined PABA and salicylate treatment in the first patient it was tried on are reported by Dr. Butt and Drs. Thomas J. Dry and Charles H. Scheffey in the Proceedings of the Staff Meetings of the Mayo Clinic.

PABA, they found in this case and in two control experiments on healthy men, increases the amount of the salicylate in the blood and therefore, presumably, gives this drug a better chance to combat the rheumatic fever.

New Preservative in Paint

► **A COLORLESS LIQUID** mixed with pigments promises new paints which resist heat, retard fire and do not darken with age. The liquid is ethyl silicate, use of which was reported to the American Chemical Society by H. D. Cogan and C. A. Setterstrom of the Mellon Institute of Industrial Research.

The new paints are expected to be particularly useful in decorating and protecting theatrical scenery, indus-

trial fabrics, furnace castings and the walls and chimneys of chemical plants.

Pigments to be used with ethyl silicate include ochre, sienna, chromium oxide, iron oxide, titanium oxide for white and carbon black for black.

Ethyl silicate has previously been used in protecting stone statues and private dwellings from weathering and for increasing the hardness of stone, brick and concrete in building construction.

Laboratory Ideas and Gadgets That Have Helped Other Chemists

Hints for Your Lab

Laboratory enthusiasts may pool their bright ideas for each others' benefit. Readers are invited to send in their "hints" for this department. Contributions become the property of CHEMISTRY. Credit will be given contributors whose ideas are accepted and "hints" will be published as time and space permits. \$2.00 will be paid for each "hint" published in this department.

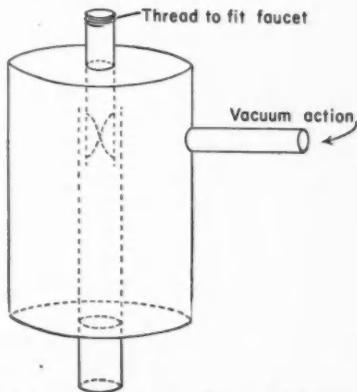
Address contribution to CHEMISTRY, Editor Hints for the Chem Lab, 1719 N street NW, Washington 6, D. C.

Vacuum Faucet Pump

► HERE ARE the plans for a very efficient vacuum faucet pump. It is made of a cylindrical spice can, $1\frac{1}{4}$ in. diameter, $2\frac{3}{4}$ in. high. Holes are drilled in the top and bottom of the can and two pieces of brass tubing, of different diameters, are fitted snugly into the holes.

The top of the can is fitted with a piece of brass tubing $\frac{5}{16}$ in. diameter, $1\frac{1}{2}$ in. long. The upper end of this tube is threaded so that a coupling can be screwed on to fit the faucet. Into the lower end of this tube a twisted piece of brass sheeting is fitted snugly, to give a swirling action to the water as it runs through. This motion creates a greater vacuum effect from the running water.

The lower end of the $\frac{5}{16}$ in. tube extends into the upper part of another piece of brass tubing, $\frac{1}{2}$ in. diameter, 3 in. long, which goes through the bottom of the can. A side tube is



inserted $\frac{3}{4}$ in. from the top of the can for attaching the rubber tubing leading to the filter flask or other piece of chemical apparatus requiring reduced pressure—GABRIEL AUGUST TURANO.

For Cleaning Glassware

► THE FOLLOWING hint has been very helpful to me in my laboratory work. In working with organic chemical reactions, it is often very difficult to clean the glassware. The regular sulfuric acid-potassium dichromate solution is usually of no value. I employ a concentrated solution of sodium hydroxide and potassium permanganate (approx. 25 grams of sodium hydroxide, 5 grams of potassium permanganate, to $\frac{1}{2}$ liter of water). Sometimes it is necessary to warm this solution and agitate it with a swirling motion for a thorough cleaning. The solution may be filtered, stored and reused.

ALAN F. ROBERTS

Distillation for Industry

► ADVANCES in distillation are pointing the way toward better industrial products at lower costs.

In a report by Dr. T. J. Walsh of the Standard Oil Company of Ohio, Cleveland, made to the Division of Industrial and Engineering Chemistry of the American Chemical Society, it is stated that despite years of study and practical application, distillation is only beginning to be treated as a science. Actually scientists and engineers know little more about the process than did the master brewers of yesterday.

Distillation, which is the process of separating substances by boiling them and condensing their vapors, has been carried out under wide ranges of temperature and pressure.

In the laboratory, distillation is used chiefly to separate relatively small quantities of some charge stock for analysis. Measurements of boiling points and refractive indexes, are the most commonly used means for determining purity of the distillates obtained.

Whether the batch consists of ten milliliters of a synthetic organic chemical or a hundred barrels of crude petroleum, the problems are essentially the same. The charge must be distilled steadily and reproducibly, the components must be separated each highly purified in a quantity sufficient for identification, there must be as little overlap as possible between

successively distilled components, and the time required for the distillation must not be excessive.

The packed column is best suited to this type of operation. Packings have been developed so that high efficiency columns can be housed within a standard laboratory building, frequently on one floor. One hundred theoretical plates in six feet of packed length are well within the range of practicability.

The operating holdup of these packings is reasonably low so that a minimum of overlap between cuts may be expected. Unfortunately, the throughput is also lower than we would like, and the time required for a precision distillation is long. A one-hundred theoretical plate distillation at one-hundred-to-one reflux ratio requires about one hundred hours on a charge sufficiently large to give one percent accuracy in the analysis of the components.

The art assists the science in this subject, and a skilled operator using special techniques can frequently complete an analysis, such as the above, in a much shorter time.

Recent progress in the field of laboratory distillation has seen the development of more highly refined equipment and better packing material. Still heads, for example, permit precise regulation of reflux or reflux ratio at all operating rates, and automatic columns make long distilling periods feasible in routine work.

Continuance of these trends will make distillation a still more useful laboratory tool. Greater reproducibility of results between laboratories and improved precision of operation within a given laboratory is possible today. It is definitely to be expected in the future.

The field of commercial distillation is distinguished by a somewhat different set of distillation problems. The purpose of operation is to concentrate according to a set of specifications a particular product for sale or further processing. Because operating conditions remain virtually constant for months or even years, continuous stills are practical. Towers up to two hundred feet high are found, and bubble plates are commonly used instead of packing.

Recent studies in tower hydraulics have disclosed in detail much of what really goes on within an operating tower, and have promoted development of more efficient stills with greater productive capacity, he continues. The lessons learned point the way to better products at lower costs.

Both equilibrium data desired in distillation and distillation calculations are receiving regular consideration, and every year additional data and new methods of applying those already on hand are being reported.

The more significant general trend of recent years has been the abandonment of the classical viewpoint in considering distillation problems. Substances that cannot be vaporized without decomposing in ordinary stills may be vaporized under the extremely low pressures of the molecular still. The non-ideality of many solutions promises to be a boon when more is known about the behavior of these non-ideal solutions. Both extractive and azeotropic distillations take advantage of the properties of non-ideal solutions.

The advances made in these relatively new fields indicate that most of distillation is still to be explored and studied. It is impossible to foresee what developments are ahead in the development of non-ideal, multicomponent stills.

Plastics Output Curtailed

► PLASTICS may be made of raw materials abundant in nature, the popular belief, but plastics making requires vast quantities of basic chemicals some of which are now in short supply. The plastics industry is dependent on these chemicals.

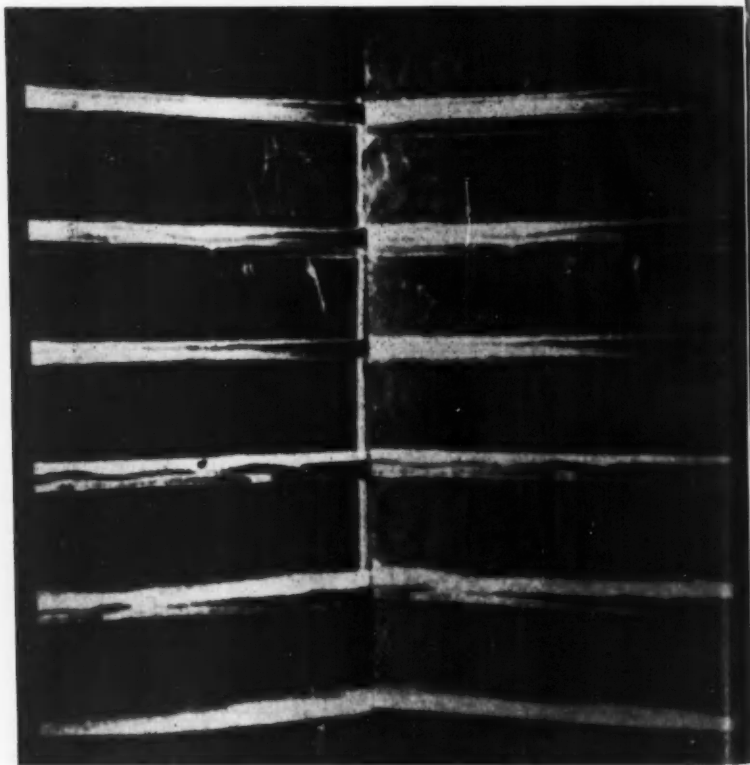
The shortage is already reflected in the output of the plastics industry, Frank H. Carman, of the Plastics Materials Manufacturers Association, told the Society of the Plastics Industry recently. He cited strikes in the coal,

steel and chemical industries as one cause of a severe curtailment in the supply of many basic materials.

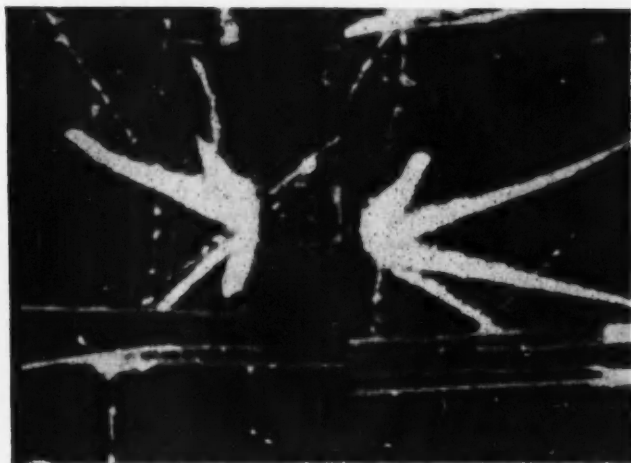
Among the chemicals now short, or facing an early shortage, are phenol, which is exceedingly tight, cresols and cresylic acids, phthalic anhydride, urea, formaldehyde and glycerine. The shortage of glycerine is due primarily to the international shortage of fats and oils and the absence of a normally large supply of copra from the South Pacific.

**Self-Portrait by Mesotron
And Alpha-Ray Explosion**

Ultimate Particle Tracks



► *ATOMIC PARTICLES took their own pictures here. Nuclear explosions were photographed with the aid of a mirror, to get a three-dimensional effect. The particle which streaks all the way down is a mesotron. The fine lines are probably made by electrons. The photographs were taken by Dr. Wilson M. Powell of the University of California.*



► ALPHA RAYS from a nuclear explosion are shown in two mirrors set at an angle. This photograph, like the one on the opposite page, comes from Dr. Powell's laboratory at California.

Hot Atoms Make New Laws

► HOT ATOMS from atomic nucleus transformations follow new rules of combination, Dr. W. F. Libby of the University of Chicago told the symposium on nuclear chemistry at a recent American Chemical Society meeting.

These hot atoms, with energies 10,000 times greater than those involved in ordinary chemical reactions, fly through solutions at enormous speed, due to recoil from such nuclear explosions as the emission of gamma rays. Such speeds make the particles collide with the atoms of the solution and ricochet like bullets hitting a wall.

New types of chemical combina-

tion, resulting from these high energy collisions, are rather simple and predictable, according to the Chicago scientist. They can be used to make a radioactive hot atom replace an ordinary atom, thus tagging a compound whose subsequent progress through chemical reactions or life processes can be watched by following its radioactive behavior.

Radioactive iodine, for example, can be made to enter the molecule of an organic compound, containing ordinary iodine. In most molecules the hot iodine will replace its non-radioactive counterpart. If, in some cases, hot iodine replaces a carbon or a hydrogen atom, the resulting compounds can be separated by chemical means.

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Years of Invention

► THE MOST productive years of inventors are not in their early youth but during their thirties and forties. This conclusion by Thomas Spooner, research engineer of the Westinghouse Corporation, is based on a statistical study of the numbers of patentable ideas put forth by men who make a career of inventing things—engineers and scientists working regularly in an industrial laboratory solving problems presented by their firm's business.

There seems to be a double peak in the average professional inventor's productive career, according to Mr. Spooner's figures. One "high" in numbers of ideas worth patenting comes in his mid-thirties, the second at about age 43. Thereafter the output of patentable inventions diminishes, though many of these staff inventors continue to be productive for a couple of decades longer.

Reporting his study in *Technology Review*, Mr. Spooner says that the period of greatest productivity, as based on the number of patent suggestions, is between 27 and 48 years of age. On the basis of outstanding inventions, the ages are 26 to 45 years of age.

Older men, he explained, frequently showed a decrease in the number of patent ideas not because of any loss of ingenuity, but because of the nature of their work. When they get into executive positions, they must devote their energies to other than strictly technical problems.

Groups considered in Mr. Spooner's survey were engineers and scientists of the Westinghouse Research Laboratories, a typical group of design engineers and a third group of engineers from a large, non-electrical research laboratory.

New Copper-Oxide Rectifiers

► THE USE OF copper oxide rectifiers to convert alternating electric current to direct current was begun just 20 years ago and millions are now in use. Research, however, has developed processes for their improvement, according to I. R. Smith, Westinghouse scientist.

The first tangible result of the research was a process of manufacture known as the vacuum-pre-anneal method. In this, the copper blanks are placed in a vacuum at high temperature, then put through normal oxidation. The cells resulting can

be operated at the same current as previous standard cells, but at twice the voltage. They were widely used during the war and had voltage output up to 3,000 volts.

Later a more simple process was discovered in which the vacuum step was eliminated. This is known as the type Q process, and the product has greater uniformity and superior aging characteristics than the earlier type. Application of these higher voltage cells have so far been largely in the broadcasting field.

U233 From Thorium; Pu Made In Nature

Uranium Rush On

►THE MOST precious material in the world today is uranium, the element from which the materials of the atomic bomb or atomic power piles can be made. It is priceless in the sense that wherever it is found it will become a monopoly of some government, until and if a United Nations atomic development authority takes over.

The most-sought-after ingredients in the earth's crust are uranium-bearing ores, such as pitchblende and carnotite.

Man's eagerness for uranium far exceeds the gold rushes of past decades. A great uranium rush is on, without fanfares of publicity, because whatever is found will become prime state and military secrets.

No exploration can be planned today without the question being raised as to whether it is not primarily a hunt for radioactive ores. It was immediately suggested that uranium is one of the principal objectives of the Byrd Antarctic Expedition now in progress.

Thorium, a commoner element in the earth's crust than uranium, becomes a raw material for the atomic age because reports transmitted to the United Nations Atomic Energy Commission by American representative, Bernard Baruch, explain that there can be made from thorium a kind of uranium that fissions and therefore can be used for atomic bombs or atomic power production.

This kind of uranium is isotope 233. It could be produced from thorium in

an atomic pile operating on the kinds of fissionable elements that have been used in atomic bombs, uranium 235 and plutonium 239. The way that uranium 233 can be formed by bombarding thorium with neutrons is very similar to the way plutonium, element 94, is made from the most plentiful and non-fissionable uranium isotope 238.

This was the reason that in proposals before the United Nations thorium as well as uranium is proposed for international control.

The chemical elements heavier than uranium have not been found in any practical quantities in nature. Yet a hint has come from Dr. Glenn T. Seaborg, co-discoverer of plutonium, that it may be premature to conclude that transuranian elements do not exist in practical amounts on the face of the earth. Further searches for useful amounts of neptunium, plutonium, americium and curium might be worth while, unlikely as that might seem from the fact that these elements had to be manufactured in order to be discovered.

Mother Nature operates her own low-power atomic pile, since during atomic bomb research it was discovered that plutonium in minute amounts is found in nature. Plutonium is formed synthetically in uranium-bearing ores such as pitchblende and carnotite, and Dr. Seaborg believes that

probably other transuranian elements are similarly formed. When uranium spontaneously fissions in nature, neutrons are given off and the nonfissionable kind of uranium is transmuted into plutonium. This reaction pro-

duces one part of plutonium in a million times a million parts of pitchblende. Almost infinitesimal as this may seem, it must be remembered that this goes on continuously in nature.

Hydrogen Peroxide for Power

► WIDER use of hydrogen peroxide in powering rockets, airplanes and submarines is foreseen.

This chemical was used by Germans during the war.

Germans did not use for these purposes the weak solution of the peroxide with which housewives are familiar, but used strong solutions concentrated to from 80% to 85% or more. They used it as primary fuel alone, but more commonly as a source of oxygen for the combustion of some other fuel such as a special diesel oil or methyl alcohol.

When hydrogen peroxide is used as a primary fuel, the hydrogen and oxygen of which it is composed become dissociated and form superheated water vapor and free oxygen. These furnish the power, but the valuable oxygen is wasted. When used with a primary fuel the oxygen permits combustion to take place, and there is no waste.

The Germans used concentrated hydrogen peroxide for 26 different weapons, a survey made by Capt. Logan McKee of the U.S. Navy showed. In experimental stages were some 40 others using the chemical. For the V-1 and V-2 bombs, the peroxide was one of the fuels used for apparatus within the bombs. Only the

heat of dissociation was employed. It was an expensive use of energy, but was so positive in action that its simplicity and reliability were worth the cost.

Airplanes powered with the peroxide to furnish oxygen for combustion gave excellent performance making it possible to climb 30,000 feet in two minutes. Peroxide-driven torpedoes were superior to other types and left essentially no wake.

The German hydrogen peroxide-powered U-boat was a true submarine that could remain submerged for long periods and had under-water speed of 25 knots. It was a thousand times more costly to operate than oil-burning U-boats from the fuel standpoint. A few were built for training purposes, then five for combat. These were never put in service, however, because there was never enough hydrogen peroxide available.

A 900-ton surface displacement submarine, nearly two and a half times larger than the five previously built, was under construction at the close of the war. The engine had never been completely assembled, thanks to bombing by the Allies. This engine is now in England for study by English and American engineers.

Robot "Fingerprint Expert" Identifies Unknown Substances

Infra-red Absorption Spectrograph

► A ROBOT "fingerprint expert" that automatically identifies unknown substances by taking their chemical "fingerprints" has been developed by a young Westinghouse research physicist to complete in minutes or hours complicated molecular studies that would require days or weeks by ordinary methods of analysis.

The new instrument, which is helping scientists to improve plastics and other insulating materials and to investigate the very structure of matter itself, is a special type of infrared spectrograph designed by Dr. Donald K. Coles of the Westinghouse Research Laboratories.

When raw materials are received for making products such as plastics, Dr. Coles explained, it is necessary to determine exactly what chemicals are present and in precisely what amounts. This infrared spectrograph harnesses infrared rays to provide the fastest and most accurate method of getting that information.

Since this type spectrograph also reveals accurately the structure of molecules, it is valuable for fundamental research in the essential makeup of such materials. It also can be used in research in the field of improved insulating materials by studying the changes that occur as the result of age and long service.

The fact that all molecules in matter vibrate at certain characteristic frequencies—millions or even billions of

times a second—gives the chance to fingerprint them.

To take advantage of this chance, Dr. Coles uses heat rays which lie in the infrared region of the spectrum and which also vibrate over a range of frequencies. When the rays are beamed through a sample substance and the frequency of the rays coincides with that of the elements in the substance, some of the infrared radiation is absorbed. Each chemical compound in this way produces an absorption pattern which appears on a chart as revealing as the lines of a fingerprint.

"When a particular wavelength or frequency of radiation is absorbed, we know that a certain structural element is present in the sample," Dr. Coles declared. "By the amount of absorption we know how much of that element is present."

To obtain these facts by ordinary chemical analysis is a tedious process. Many of the answers the infrared spectrograph can obtain in minutes or hours would take a group of chemists days, weeks, or months to determine.

How It Works

Although infrared absorption spectroscopy cannot be used to study metals—such studies being the field of so-called "emission" spectroscopy—its value as an analyzer of liquids, gasses and many solids has been proved in laboratory tests.

A sample of the material to be analyzed is placed in a holder in front of

a silicon-carbide rod. When the rod is heated to an incandescent glow, it produces infrared rays which are beamed through the sample material. This beam zigzags along a 30-foot path guided by highly polished mirrors and two large prisms. The prisms spread the beam into a wavelength pattern or spectrum much as raindrops turn a beam of sunlight into a rainbow.

At the end of the 30-foot journey, a metal slit allows one wavelength at a time to pass through to sensitive receivers which convert the ray into electric current, amplify it, and electronically record that portion of the fingerprint on a chart in terms of current intensity.

This procedure is continued automatically for each wavelength of the infrared spectrum so that the final fingerprint of a sample reveals on the chart the structure of the sample substance.

Infrared spectrographs first came into important use during the war to speed molecular engineering such as that involved in the development and volume production of synthetic rubber, high octane gasoline, new plastics and synthetic chemicals. Dr. Coles' instrument, however, marks an advance in spectroscopy technique by being fully automatic and recording the complete fingerprint of a sample by the push of a button.

The mirrors in the spectrograph rotate during an analysis to direct the particular wavelength of infrared radiation toward the exit slit. Even the slit openings automatically change in size to make room for the longer or shorter wavelengths to pass. The movements are synchronized automatically to occur at the exact moments necessary.

The two four-by-six inch prisms spread the infrared beam into a wavelength pattern and prevent any radiations from straying into the wrong path. The fact that two prisms are used makes it possible to disperse or spread the spectrum twice as wide as if only one were employed, as in the case of the single "monochromator." This instrument, using two prisms and two sets of mirrors, is called a "double monochromator" and makes possible more accurate results.

Whereas infrared absorption spectroscopy identifies molecules, which are groups of atoms, one of its electronic cousins called emission spectroscopy measures atoms themselves. This explains why absorption methods are used to analyze complex chemical compounds where the structure of the molecules is important while emission methods are suited to the analysis of metals where the presence of the atom is the chief factor.

Emission spectroscopy reverses the method used in infrared absorption technique. In using the infrared spectrograph, the silicon-carbide rod is heated and the resulting infrared rays are passed through the unheated sample. The amount of rays absorbed by the material then can be measured. In emission methods, however, the sample material itself is heated to some 10,000 degrees Fahrenheit. This terrific heat accelerates movement of the atoms, separating one element from another and causing each element to emit light of a definite wavelength. By analyzing the emitted light rays, the type and quantity of the element is determined.

The infrared spectrograph also sup-

plements but does not replace another cousin, the new member of the electronic family—the mass spectrometer. This latter instrument in addition to its task in nuclear research is used

widely in the synthetic rubber and petroleum industries to determine the molecular structure by “weighing” or sorting molecules and parts of molecules according to their mass.

New Light on “Coronium”

► A NEW CHAPTER in one of the major astronomical mysteries was written when the American Astronomical Society was told at a recent meeting that the red “coronium” spectrum line of light has been found in the sun itself, indicating that the sun has regions of much higher energy than previously suspected.

The researches of Dr. Leo Goldberg, director of the University of Michigan Observatory, detected the broad and fuzzy absorption line of the solar disk that is identical with one of the most characteristic lights of the filmy, beauteous corona seen only during natural or artificial eclipse of the sun.

Discovery of this line and prominent green lines at solar eclipses in

the last century caused astronomers to believe that a chemical element they named coronium existed only in the heavens and not on earth. Not until 1940 did Dr. Bengt Edlen, Swedish astronomer, prove that the strange element was really common earth substances, iron, nickel and calcium, in highly excited states.

Discovery in the sun of the absorption line of iron from whose atoms nine electrons have been stripped is confirming incidental proof that there is no mysterious coronium.

Dr. Goldberg's findings, made in cooperation with Drs. R. R. McMath and O. C. Mohler of the McMath-Hulbert Observatory, may mean that gases are bubbling up from the sun's interior into its bright outer envelope.

Deuteron Beam From Supercyclotron

► FOR THE FIRST time in the world's history, a 200,000,000 electron volt beam of heavy hydrogen atomic hearts has been produced. This was the first experiment with the 4,000-ton supercyclotron just put into operation at Berkeley, Calif.

Dr. Ernest Lawrence, Nobelist and cyclotron inventor, reported that the deuteron beam was used to bombard beryllium and that a sharp, intense beam of high energy neutrons resulted from the bombardment.

Engineering work by the University of California radiation crew headed by Prof. Robert L. Thornton and William Brobeck, called “brilliant” by Dr. Lawrence, solved operating difficulties more quickly than expected.

Several months of experiments were planned with the giant instrument without major changes. Scientists predicted results more important than the previous ones with cyclotrons. The atomic bomb element, plutonium, was made in a smaller cyclotron.

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